Theory of fluorescence excitation spectra using anharmonic-Coriolis coupling in \( S_1 \) and internal conversion to \( S_0 \). II. Application to the channel three problem in benzene for the \( 14^11^2 \) band

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Rotational lines in the fluorescence excitation spectra of the \( 14^11^2 \) band of the first excited singlet state \( (S_1) \) of benzene are calculated for various \( J \) and \( K \). For this purpose, perturbation theory is used to obtain an “eigenstate” in \( S_1 \). Internal conversion to \( S_0 \) via Franck-Condon (FC) factors is then calculated. A search procedure is used to obtain the important contributors to this \( S_1 \) state and to this internal conversion process \( S_1 \rightarrow S_0 \) using the perturbation theory coefficients and the FC factors in the evaluation function. At low \( J \), the calculated lines with \( K=0 \) are sharp, other lines being broadened and diminished in intensity. The calculated \( K=0 \) lines have a linewidth proportional to \( J(J+1) \). For high \( J \), the lines with \( K=J \) remain sharp, the other lines being broadened and diminished in intensity. These various results are in general agreement with the experimental findings. The onset of channel three in benzene occurs in the present mechanism via anharmonic-Coriolis coupling in the \( S_1 \) state plus internal conversion to \( S_0 \). The calculations suggest that, at low \( J \), parallel Coriolis coupling causes mixing of the in-plane mode-excited “light state” with in-plane modes that are anharmonically coupled to out-of-plane modes. Dark states with certain excited out-of-plane mode contributions possess large FC factors for the internal conversion to \( S_0 \). At high \( J \), on the other hand, the in-plane modes are coupled directly to these out-of-plane modes by perpendicular Coriolis coupling. Paths involving two perpendicular Coriolis operators are important at high \( J \) in the present calculation—their matrix elements are larger at high \( J \) and so they become more competitive relative to purely anharmonic coupling operators. Such two-Coriolis paths at high \( J \) are expected to yield multiple excitation in the out-of-plane modes and further enhance the internal conversion. The perpendicular Coriolis coupling is least at \( J=K \) and so these lines survive at high \( J \). Two-Coriolis operator paths are calculated to be relatively unimportant at low \( J \). The present calculations, using the same electronic matrix element, account for both the low \( J_K=0 \) and high \( J_K=J \) acts of lines being the dominant ones. Aspects regarding further study are discussed.

I. INTRODUCTION

In studies of fluorescence of the first excited singlet state \( (S_1) \) of benzene, a sudden drop in fluorescence intensity occurs for energies somewhat in excess of 3000 cm\(^{-1}\) above the \( S_1 \) electronic origin. Historically, the unknown decay channel responsible for this cutoff has been termed “channel three,” and has been a topic of experimental and theoretical research for the past 25 years.\(^{1-6}\) While it was first described some time ago,\(^{1-6}\) it has since been studied using high resolution one-photon\(^{16}^{24}\) and Doppler-free two-photon electronic spectroscopies.\(^{9,10}\) The latter techniques have led to rotationally resolved electronic absorption spectra of excited state benzene.\(^{7-22}\)

At low vibrational energies, below the onset of the channel three region and where benzene acts in the small molecule limit, it has been possible to excite various rovibrational quantum states and observe both the expected rovibrational lines and isolated avoided crossings (resonances) with other dark states.\(^{7,10,19,26}\) These resonances reflect details of the couplings of the zeroth order states. Earlier, we treated such avoided crossings theoretically using perturbation theory, in the form of the van Vleck contact transformation, employed commonly in the treatment of molecular vibration-rotation problems. The coupling terms used involved principally cubic anharmonicities and various order Coriolis terms.\(^{23}\) Typically, quasiresonant states differing in four vibrational quanta were coupled by some few hundred state-to-state paths, the number depending on the states, and third order perturbation theory\(^{24}\) was employed. In that study, the energy in excess of the zero point energy was 1570 cm\(^{-1}\). The results were in reasonable agreement with the experiments.

At higher vibrational energies, namely in the channel three region, the rotationally resolved spectra show a loss of intensity for individual lines, indicating a fast decay process which competes successfully with the fluorescence.\(^{8,10,12,14-16,22}\) Most of the individual rotational lines are then absent. For example, for the \( 14^11^2 \) band\(^{25} (3412 \text{ cm}^{-1}) \), at low values of \( J \) only the \( K=0 \) lines remain.\(^{15,22}\) (For example, the \( J_K=0 \) to \( 14 \) lines are depicted in Ref. 15.) Their width is dependent on the rotational quantum number \( J \). At high values of \( J \), only the \( K=J \) lines survive to any major extent.\(^{15}\) (For example, in Ref. 15, the \( J_K = 27 \rightarrow 45 \) lines are depicted.) Close to the threshold of
In the present study, the important $S_1$ component of the relevant eigenstate in benzene is calculated using perturbation theory containing, among others, cubic anharmonic coupling and various Coriolis interaction terms. Zeroth order states in $S_1$ which differ in up to nine quanta from the light state in $S_1$ are included as contributors. A result is then obtained for the $S_0$ contribution to the molecular eigenstate by using the kinetic energy operator for IC to the ground electronic state $S_0$. The calculation utilizes, in addition to the perturbation theory in $S_1$, an "artificial intelligence" (AI) search among the many contributing FC active states in $S_1$ and among the states to which they are coupled in $S_0$. Fluorescence excitation spectra are then calculated and compared with experiment for the $14112$ vibronic band in $S_1$. This band, at $3412 \text{ cm}^{-1}$, is well within the channel three region. Rotationally resolved data for this band have been obtained mainly by Riedle, Neusser, and Schlag. The present paper is an application of the treatment outlined in the previous paper (part I).

The detailed expression contains an electronic internal conversion matrix element. The latter could either be evaluated ab initio, or, as in the present paper, evaluated from the experimental slope of the plot of linewidth vs $J(J+1)$ for the $K=0$ spectral lines at low $J$, and then used to make predictions of other properties of the system. Its value, so estimated, is then compared with an ab initio value.

In a procedure different from the present one, Dietz and Fischer used an analytical approach for IC in the $14112$ state of benzene. They assumed a statistical distribution of energy and an equidistant spacing of zeroth order dark states in $S_1$, coupled to the $14112$ light state, a single value for a Coriolis coupling parameter and one for a cubic anharmonic parameter. In another study, Hornberger and co-workers assumed a statistical distribution of the vibrational energy in $S_1$ to calculate the internal conversion rates to $S_0$ as a function of vibrational energy. Experimental evidence against a statistical model has been given by Yoshihara and co-workers who found that the short-time spectra (before collisional relaxation) are characteristic of the level initially selected.

Details of the procedure specific to treating the $14112$ band of benzene are given in Sec. II. Results of the treatment of the $14112$ band are described in Sec. III, including the use of dark states in $S_1$, the rotational lines and fluorescence excitation spectra at low and at high $J$, and the robustness of calculated spectral lines with respect to random shifts of vibronic band origins in the $S_1$ state. These features of the results are discussed in Sec. IV, where a comparison is made with experiment. A calculation of the distribution of the importantly contributing dark states in the $S_1$ eigenstate is also given for comparison with a statistical model used in Refs. 32–34 and 36. Some concluding remarks are given in Sec. V.

II. PROCEDURE FOR THE $14112$ $S_1$ BAND

A. Overview

In part I, the model in which a single molecular "eigenstate" of the $S_1$ Born–Oppenheimer Hamiltonian is coupled via internal conversion to a quasicontinuum of $S_0$ rotational–vibrational states was discussed. The $S_1$ eigenstate $\Psi_{S_1} = \psi^e_{S_1} \psi^v_{S_1}$ can be written in terms of a linear combination of zeroth order rigid rotor harmonic oscillator (RRIHO) states $\psi^v_{S_1}$,

$$\psi^v_{S_1} = \sum_i c_i \psi^v_{S_1,i}. \quad (2.1)$$

The $c_i$'s are obtained by perturbation theory, using the $|14112;J,K\rangle$ "light" state as the zeroth order wave function, a state that is accessible by two-photon absorption from the $S_0$ ground state.

For the two-photon absorption of benzene, the experimental data leading to the $14112$ band are consistent with a $Q$ branch ($\Delta J = \Delta K = 0$) of the electronic transition. By group-theoretic and other arguments, only the state $|14112;J,K\rangle$ was a suitable candidate for the excited ("light") state, when the other background RRHO states in $S_1$ at an energy near the $14112$ band ($3412 \text{ cm}^{-1}$) were considered.

The states $|14112;J,k\rangle$ are doubly degenerate. $k$, whose magnitude is $K$, may be positive or negative. Since typically these two states do not couple with each other except in high order (such coupling matrix elements are not considered here), each such state $|14112;J,k\rangle$ may be considered nondegenerate for our purposes, and so we use nondegenerate perturbation theory in determining the $S_1$ eigenvector.

For $K > 0$ in the light state, with a single Coriolis operator (as in the low $J$ calculations), only states with the same sign of $k$ as the light state are available in $S_1$, regardless of whether positive or negative $k$ values are considered. Since the relevant coupling matrix elements and zeroth order energies of states differing only in the sign of $k$ are identical, it is sufficient to consider, in the present calculations, only positive values of $k$ for the initial state in the perturbation theory. For these states, $K = k$ and so the magnitude $K = |k|$ is used in the notation in this paper.

When $K=0$ in the light state, access to states with $k=1$ and $k=-1$ occurs via perpendicular Coriolis coupling and they are explicitly included. Since zeroth order states with $k=1$ and $k=-1$ (and $k=2$, $-2$) do not have the same energy as the initial ($k=0$) zeroth order state, nondegenerate perturbation theory can be used.

The wave function $|\psi^v_{S_1}\rangle$ can be expressed in terms of a projection operator $P$ and the unperturbed state $|14112;J,K\rangle$,

$$|\psi^v_{S_1}\rangle = P|14112;J,K\rangle. \quad (2.2)$$
Using nondegenerate perturbation theory, the part of \( P \) operating on the \(|14^{1}1^{2}, J, K)\) subspace is

\[
P = P_0 + \frac{Q_0}{a} V_S P_0 + \frac{Q_0}{a} V_A - \frac{Q_0}{a} V_S P_0 + \cdots, \tag{2.3}
\]

where \( P_0 \) and \( Q_0 \) are projection operators

\[
P_0 = \langle \psi_{S_1}^{I_0} | \psi_{S_1}^{I_0} \rangle,
\]

\[
Q_0 = \sum_{\nu \neq I_0} \langle \psi_{S_1}^{I_0} | \psi_{S_1}^{\nu} \rangle \langle \psi_{S_1}^{\nu} | \psi_{S_1}^{I_0} \rangle,
\]

and \( \nu \) denotes \( E_0 - H_0 \). \( E_0 \) is the eigenvalue for the zeroth order light state in \( |S_1, 14^{1}1^{2}, J, K)\), denoted in Eq. (2.4) by \( |\psi_{S_1}^{I_0} \rangle \). The coupling of the light state by perturbation terms \( V_S \) to a manifold of \( S_1 \) RRHO states is treated in the present paper using the vibration–rotation Hamiltonian discussed in part I.\(^{43} \) Internal conversion couplings to \( S_0 \) are computed using the golden rule and a sum involving these zeroth order components of the \( S_1 \) eigenstate.

The nonradiative linewidth (full width at half height) \( \Delta_{nr} \) due to IC is given approximately in part I, in units of \( \pi - 1 \), by

\[
\Delta_{nr} = \frac{2}{\Delta} \sum_{\nu} |V_{IC,\nu}|^2, \tag{2.6}
\]

where \( S \) is the \( S_1 \) eigenstate \( |\psi_{S_1}^{I_0} \rangle \) in Eq. (2.2) (with RRHO components \( \psi_{S_1}^{\nu} \)), and \( \nu \) labels RRHO states in \( S_0 \) in a narrow energy range \( \Delta \) centered at the energy of the zeroth order light state in \( S_1 \). The presence of the \( S_0 \) RRHO states (instead of the \( S_0 \) eigenstates) in Eq. (2.6), and the approximate formalism leading to that aspect, are discussed in part I. In Eq. (2.6) \( V_{IC,\nu} \) involves the nuclear kinetic energy operator

\[
V_{IC,\nu} = -\langle \psi_{S_1}^{I_0} | \frac{\partial}{\partial Q^2} \rangle | \psi_{S_0}^{\nu} \rangle \langle \psi_{S_0}^{\nu} | \frac{\partial}{\partial Q^2} | \psi_{S_1}^{I_0} \rangle. \tag{2.7}
\]

Because it is much less important, a term involving \( \partial^2 / \partial Q^2 \) operating only on \( \psi_{S_0}^{\nu} \) was omitted here.\(^{49} \) In Eq. (2.7), the electronic matrix element is regarded as the value in the \( Q \)-centroid approximation,\(^{50} \) and the vibrational matrix element includes the usual product of FC factors (the rotational matrix element \( I, K \mid J, K) \) is, of course, unity. In Eq. (2.7), the normal mode \( Q_\rho \) is of the proper symmetry to promote the transition to \( S_0 \). Since \( S_0 \) is of \( A_{1u} \) symmetry and \( S_1 \) of \( B_{2u} \) symmetry, the promoting modes in the case of benzene are of \( b_{2u} \) symmetry, namely, \( Q_{14} \) and \( Q_{15} \). For the present, the same value of the electronic matrix element is assumed for both choices of the inducing mode \( Q_\rho \).

The rotational lines in the fluorescence excitation spectra under collision-free conditions are calculated as Lorentzians whose width and intensity are determined by the IC rate, the fluorescence decay rate, and ground state statistical factors. The relative intensities of the individual lines were given in part I as

\[
I_{J,K}(E - E_{S_0}) = I_{J,K} L. \tag{2.8}
\]

where \( I_{J,K} \) is the integrated relative intensity of the \( J, K \) line given by

\[
I_{J,K} = \phi_f |c_f(J', K')| c_d C_{\text{rot}} C_{\text{vib}} (J', K', K'' | J'' K'')^2 (2J' + 1) \times f_{\text{ncu}}(J'', K''), \tag{2.9}
\]

\[
\phi_f = \Delta_f / (\Delta_f + \Delta_{nr}) \tag{2.10}
\]

and \( L \) is a Lorentzian function

\[
L = \frac{1}{2\pi} \frac{(\Delta_f + \Delta_{nr})}{(E - E_{S_0})^2 + (1/4) (\Delta_f + \Delta_{nr})^2} \tag{2.11}
\]

which, when integrated over a “line” for a particular \( S_1 \) \( J, K \) state, yields unity. In Eqs. (2.9) and (2.10), \( \phi_f \) is the fluorescence quantum yield of the given \( J, K \) state; \( c_d \) denotes the coefficient of the zeroth order light state in the \( S_1 \) quasieigenstate \( \psi_{S_1}^{I_0} \); \( c_f \) is the electronic matrix element\(^{51} \) for the relevant component of the two-photon absorption (TPA) tensor from state \( S_0 \) to \( S_1 \); \( C_{\text{rot}} \) is the vibrational matrix element of the appropriate component of the TPA tensor\(^{51} \) for the transition from the ground state zero vibrational level to the \( 14^{1}1^{2} \) light vibrational state;\(^{51} \) \( |C_{\text{rot}}(J', K', J'', K'')|^2 \) is a weighted sum of squares of rotational matrix elements, possibly complex, for several components of the TPA tensor;\(^{51} \) \( f_{\text{ncu}}(J'', K'') \) is the nuclear spin statistical factor for the ground state species;\(^{52-54} \) \( f_{\text{Boltz}}(J'', K'') \) is the Boltzmann weighting factor for the ground state at the rotational temperature of the experiment; and \( L_f \) is the linewidth due to fluorescence and is, in general, small compared with \( \Delta_{nr} \) in the channel three region. \([\phi_f \text{ in Eq. (2.10) is typically of order of } 10^{-3} \text{ or less in that region.}] \) \( E_{S_0} \) is the energy of the quasieigenstate in \( S_1 \). Values of the calculated nonradiative linewidth \( \Delta_{nr} \), fluorescence quantum yield \( \phi_f \), and \( I_{J,K} \) are given in Sec. III. The correction of Eq. (2.11) for pressure broadening \( \Delta_{nr} \) and for instrumental broadening is noted later in Sec. II D.

### B. AI search algorithm for \( S_0 \) RRHO states

The “AI search” employed was a very straightforward one—states in \( S_1 \) within \( \pm 1000 \text{ cm}^{-1} \) of the zeroth order \( J, K \) state (the \( S_1 \) state must have the same \( J \) and have \( K \) within two of that for the zeroth order state) were selected and ordered with respect to the net number of vibrational quanta \( q \) exchanged, and with respect to the net difference in \( K \) (so determining the maximum number of perpendicular Coriolis operators in a path). Paths leading to the \( S_1 \) states were found, there being no restriction on the energies of the intermediate \( S_1 \) tier states in the search. For each such “final” state, the Franck–Condon factors to the \( S_0 \) states in a small preselected energy interval about the zeroth order state were calculated. Only the states in \( S_1 \) and \( S_0 \) which yield a preassigned value of an evaluation function (E.F.) given below were retained in the search and so contributed to \( \Delta_{nr} \). Details specific to the \( 14^{1}1^{2} \) band in benzene are given here. All vibrational states considered in \( S_1 \) are of ungerade parity, since only they may couple with the \( 14^{1}1^{2} \) state, which is of \( b_{2u} \) symmetry.
Among the "acceptor modes," 11 are considered "active" in IC (i.e., $\Delta v_{\alpha} \neq 0$), namely, the modes $Q_1(a_{1g})$, $Q_2(b_{2g})$, $Q_3(b_{2u})$, $Q_6(e_{2g})$, $Q_{10}(e_{1g})$, $Q_{11}(e_{2u})$, $Q_{14}(e_{2u})$, $Q_{15}(e_{2u})$, $Q_{17}(e_{1u})$, and $Q_{18}(e_{1u})$. The nine remaining modes ("inactive") essentially do not change their excitation, i.e., $\Delta v_{\alpha} = 0$, during internal conversion. A mode is placed on the inactive list when it yields (after a search of quasiequilibrium states in $S_0$) small overlap integrals and/or too few states in $S_0$. These inactive modes and their symmetries are $Q_4(a_{1g})$, $Q_5(e_{1g})$, $Q_8(e_{2g})$, $Q_{12}(b_{1u})$, $Q_{13}(b_{1u})$, $Q_{16}(b_{2u})$, $Q_{19}(e_{1u})$, and $Q_{20}(e_{1u})$.

The modes $Q_6$ to $Q_{10}$ and $Q_{16}$ to $Q_{20}$ are doubly degenerate; $Q_1$ is the only totally symmetric (a$_{1g}$) active mode and $Q_2$ is the only totally symmetric inactive mode. There are, in addition, ten nontotally symmetric active (NTS) modes and eight NTS inactive modes. The allowed values of $\Delta v_{\alpha}$ for both active and inactive acceptor modes are given in part I.$^{43}$

In the case of benzene, the additional restriction for degenerate modes $Q_4$ ($Q_6$-$Q_{10}$ and $Q_{16}$-$Q_{20}$)

$$\Delta I_4 = 0$$

(2.12)

reduces a 30-dimensional search for $S_0$ states to a 20-dimensional search,$^{52}$ since for each of the ten degenerate modes, the vibrational quantum number $I$ remains constant in proceeding from $S_1$ to $S_0$.

Since the quantum state for all inactive modes is specified, one need not sum over these modes when searching for states in $S_0$ with large FC overlap to a given RRHO basis state in the $S_1$ eigenvector. As already noted, there were nine such modes and so the 20-dimensional search is now further reduced to an 11-dimensional search.

This 11-dimensional search in the $S_0$ manifold was performed for the 11 active modes. In the search, the low frequency out-of-plane mode $Q_4$ was restricted to having at least 24 quanta in $S_0$, since otherwise, the FC factor was found to be quite small. In addition to satisfying the selection rules for individual normal modes,$^{43}$ a prospective rovibronic state in the $S_0$ manifold was required to satisfy several additional criteria in order to be selected:

(1) The state in $S_0$ should lie in a specified narrow energy range $\Delta$ centered about the $S_1$ energy $E_{S_1}$ of the $S_1$ quasieigenstate. In practice, it is sufficient to choose as the energy center the zeroth order energy of the RRHO state in $S_1$ that is the dominant contributor to the $S_1$ eigenvector. As already noted, there were nine such modes and so the 20-dimensional search is now further reduced to an 11-dimensional search.

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(1) The state in $S_0$ should lie in a specified narrow energy range $\Delta$ centered about the $S_1$ energy $E_{S_1}$ of the $S_1$ quasieigenstate. In practice, it is sufficient to choose as the energy center the zeroth order energy of the RRHO state in $S_1$ that is the dominant contributor to the $S_1$ eigenvector, which is the light state in the present case. The narrow range $\Delta$ in Eq. (2.6) is taken to be 0.03 cm$^{-1}$. The zeroth order energy is 41 502 cm$^{-1}$ plus the rigid rotor energy $B_J(J+1)-\frac{1}{2}kT$, 41 502 cm$^{-1}$ being the sum of the difference in electronic origins 38 086 cm$^{-1}$ plus the zeroth order vibrational energy 3416 cm$^{-1}$ above the zero-point energy in $S_1$.$^{56,57}$ In the statistical limit, $\Delta v_{\alpha}$ should be independent of $\Delta$, for small $\Delta$, and the exact placement of the energy "window" should be unimportant, since in $S_0$, there is a large enough density of states with similar numbers of states and coupling strength, regardless of the precise placement of the energy center.

(2) Symmetry criteria specific to the promoting modes should also be satisfied. In benzene, $Q_{14}$ and $Q_{15}$ are the promoting modes. When $Q_{14}$ is the promoting mode, then

$$\Delta v_{14} = \pm 1, \pm 3, ..., \text{ and } \Delta v_{15} = 0,$$

(2.13)

since $Q_{15}$ is inactive and since there is a $\partial/\partial Q_{14}$ operator in the integrand of the mode $Q_{14}$ overlap integral, thereby switching the even-only rule for nontotally symmetric active modes$^{43}$ to odd only. When $Q_{15}$ is the promoting mode, one has, instead,

$$\Delta v_{14} = 0, \pm 2, \pm 4, ..., \text{ and } \Delta v_{15} = \pm 1,$$

(2.14)

since mode $Q_{14}$ is active and mode $Q_{15}$ is subject to the odd-only rule due to the $\partial/\partial Q_{15}$ operator, and being inactive is further restricted to the smallest allowed changes in its quantum number ($\pm 1$). In the search algorithm, $Q_{14}$ and $Q_{15}$ are alternately allowed to be the promoting mode.

(3) A tentatively selected rovibronic state in $S_0$ must have a sufficiently large FC overlap integral with a dark zeroth order (RRHO) state in the $S_1$ eigenvector that provides access to it via IC. In the evaluation function, given below, account is also taken of the contribution $c_i$ of the $S_1$ RRHO state to the $S_1$ "eigenstate."

Each of the above selection criteria was encoded in separate subroutines which return to a 11-fold loop if the given criterion is not satisfied. A zeroth order state in $S_0$ was accepted when all of the above criteria were satisfied, provided the evaluation function

$$E_F = |c_i(\Psi_{S_1}^{\ast} | \partial/\partial Q_{j} | \Psi_{S_0}^{\ast} )|^2$$

(2.15)

was equal to or exceeded a specified minimum value. In the present work for $J_K=6_4$, this minimum value was chosen to be $1.0 \times 10^{-12}$ cm$^{-1}$. In the typical case of an accepted $S_0$ state, the matrix element in Eq. (2.15) was $\sim 1 \times 10^{-10}$ cm$^{-1}$ and $c_i$ was $\sim 0.01$. Cut-off values for other $J_K$ were determined by comparing the $c_i$'s for such a $J_K$ with their corresponding values (for the same $S_1$ vibrational state $i$) when $J_K=6_4$ and adjusting the cutoff in proportion to a mean value for this ratio.$^{58}$

The disposition of energy among the $S_0$ normal modes was also calculated, even though it is not needed for the observables calculated in the present paper. The results could then be compared with those predicted$^{35-36}$ from statistical type models. To obtain the energy disposition among modes, a summation over $S_0$ states was made, each $S_0$ state weighted by the product of the coefficient $c_i$ of the $S_1$ RRHO state in the $S_1$ eigenvector that the $S_0$ state couples to, with the FC factor for that coupling via IC, and with the amount of energy in each mode. Specifically, in the present calculation, the fraction of vibrational energy in mode $Q_k$ in the $S_0$ electronic state is

$$f_k = \frac{\sum_j \sum \Psi_{S_1}^{\ast} |Q_{S_0;j}^{\ast} |(\Psi_{S_1}^{\ast} | \partial/\partial Q_{j} | \Psi_{S_0}^{\ast} )|^2 n_{k;0} \omega_k}{\sum_j \sum \Psi_{S_1}^{\ast} |Q_{S_0;j}^{\ast} |(\Psi_{S_1}^{\ast} | \partial/\partial Q_{j} | \Psi_{S_0}^{\ast} )|^2 n_{k;0} \omega_k},$$

(2.16)

where $\Psi_{S_1}^{\ast}$ is the $i$th $S_1$ RRHO state that provides access to the $j$th RRHO state in $S_0$, $\Psi_{S_0;j}^{\ast}$; $c_i$ is the coefficient of this $i$th state in the $S_1$ quasieigenstate; and $n_{k;0}$ is the vibrational quantum number in $S_0$ for state $j$ for mode $Q_k$ with frequency $\omega_k$ in $S_0$. The sum over $p$ is over the pro-
moting modes $Q_{1s}$ and $Q_{1s}$, as noted earlier. Data used in the evaluation of integrals in Eq. (2.7) are given in Appendix A. For notational brevity, $c_i^2$ is used throughout this paper, as in Eq. (2.16), instead of $|c_i|^2$. In the present paper, all matrix elements and hence all $c_i$ are real.

C. Calculation of the $S_1$ "molecular eigenvector"

The $S_1$ RRHO states appearing in Eq. (2.1) for the $S_1$ eigenvector are found as perturbation corrections to the zeroth order light state $|14^11^2J,K\rangle$ upon using the terms in the $S_1$ vibration-rotation Hamiltonian to couple the various zeroth order states. A discussion of the coupling is given in part I.43

The vibration-rotation Hamiltonian used in the calculation of $c_i$, the coefficient in the $S_1$ eigenvector, is expanded according to the perturbation order of the vibrational and rotational operators59–65

$$H = \sum_m \sum_n \lambda^{m+n-2} H_{mn}. \quad (2.17)$$

Here, $\lambda$ is a perturbation parameter and $m$ and $n$ denote the degree of vibrational and rotational operators, respectively. Specific terms in Eq. (2.17) relevant to benzene are discussed in part I.43

In the algorithm that couples $S_1$ states by terms in the rotational–vibrational Hamiltonian equation (2.17), no energy restriction was imposed on the intermediate $S_1$ dark states in a path. The final $S_1$ dark states which directly undergo IC were restricted to $\pm 1000$ cm$^{-1}$ window. (A refinement of the present numerical procedure would include a study of imposing and varying specified limits on the energies of the selected RRHO $S_1$ states.)

To provide access to the vast majority of dark zeroth order states in $S_1$ at this excess vibrational energy (3412 cm$^{-1}$), an exchange of about 11 vibrational quanta would have been needed (cf. Table VIII given later, which contains a count of $S_1$ states in a $\pm 20$ cm$^{-1}$ window). A test for "convergence" in a practical sense was made by increasing the number of dark states used in $S_1$ to see if the "observable" $\Delta_0$ reached some limiting value. The dark states in $S_1$ that were found in the calculation to provide most of the FC coupling to $S_0$ differed from the $14^11^2$ state in five or six vibrational quanta. In the final calculations, the perturbation expansion48 was truncated in the determination of the $S_1$ "molecular eigenvector" $\Psi_{S_1}$ such that a maximum net exchange of nine vibrational quanta was allowed.

The vibrational potential energy in the Hamiltonian was expanded as a polynomial in normal coordinates. The kinetic energy has only terms quadratic in their conjugate momenta with coefficients which are constants. (Alternatively, the potential could be expanded in curvilinear coordinates.) Ab initio cubic curvilinear constants have been calculated for benzene56,67 and are equal to the corresponding cubic anharmonic constants in a normal mode (rectilinear) description, e.g., as noted in Ref. 23. While they were obtained only for the $S_0$ state, the anharmonic constants are needed for $S_1$ and they were approximated by those in $S_0$ as before.23

Individual terms in $H$ up to third order were included. [In the projection operator $P$ in Eq. (2.2), terms can occur more than once.] In the first order terms, the $H_{21}$ Coriolis operator, the centrifugal distortion operator $H_{12}$, and the cubic anharmonicity operator $H_{30}$ were included. The ab initio cubic force field is employed and the calculation of other relevant molecular constants are described in Appendix A.

Second order terms in $H$ used in the calculations include the Coriolis operator $H_{31}$, a centrifugal distortion operator $H_{22}$, and the term quadratic in vibrational angular momenta $\mathbf{P}_D^2$, $H_{40}$. The quartic anharmonicity $H_{40}$ was not included; it was unavailable at the time.68 The only third order term included is the Coriolis operator $H_{41}$.

The symmetry requirements for nonzero cubic force constants in $H_{30}$ and for Coriolis coupling coefficients in $H_{21}$ are well known.37 The symmetry restrictions for the higher order Coriolis terms $H_{31}$ and $H_{41}$ for benzene were derived individually and are given in Appendix B of Ref. 23. For example, the distortion coordinate in $H_{31}$, and the two in $H_{41}$, may be of the $a_2g$ or $a_1g$ irreducible representations.

When doubly degenerate modes are excited in a dark RRHO $S_1$ state, as in the present case, not every $l$ substate within that vibrational parentage is coupled to the $|14^11^2J,K\rangle$ light state. For example, there are 16 $l$ substates of parentage $1^610^11^61^6$, of which only six couple with the light state $|14^11^2J,K\rangle$ according to the selection rule60

$$-\Delta k + \sum_l a_l \Delta l + \frac{1}{2} N \sum_l \Delta v_l \mathbf{P}_D N. \quad (2.18)$$

This rule reflects conservation of the overall rovibronic symmetry with respect to a $C_N$ operation in a radiationless transition.69,70 The $C_N$ operation being about the principal symmetry axis for a symmetric top (here $N=6$).71 In Eq. (2.18), $p$ is an integer, the sum over $l$ is over all modes belonging to $b$-type irreducible representations ($b_{1g}$, $b_{2g}$ etc.), and the sum over $t$ is over degenerate modes that change their respective $l_t$ values by $\Delta l_t$ with $a_{l_t}=1$ for an $e_l$-type mode ($e_l \epsilon e_{1p}$) and $a_{l_t}=2$ for an $e_l$-type mode ($e_l \epsilon e_{2p}$), in proceeding from the light to the dark state. For a given $\Delta k$, Eq. (2.18) provides the allowed $\Delta l$'s for IVR in $S_1$.

All calculations are for an initial $k=0$, and so $k$ in Eq. (2.18) could be replaced by its absolute value $K$, except for $k=0$ initially. Here, we retain the $k$ in Eq. (2.18) since $k=-1$ and $k=-2$ can occur along a selected path ($k=-2$ only when paths with two perpendicular Coriolis operators are included). As an example of Eq. (2.18), for coupling to the dark states of parentage $1^69^11^61^6$, we have $\Delta K=0$, since $\Delta K=\pm 1$ does not satisfy Eq. (2.18) for the allowed values of $\Delta l_t$. Regardless of the virtual states that provide access to these $1^69^11^61^6$ states when there is at most one Coriolis operator in any "path," that operator must be a parallel Coriolis one ($\Delta K=0$). When there
are two Coriolis operators in a path, an overall change of \( \Delta K = 0 \) is still possible by two \( \Delta K = \pm 1 \) steps, and also by two perpendicular Coriolis operators, one leading to \( \Delta K = \pm 1 \) and the other to \( \Delta K = \mp 1 \).

The RRHO energies are given by

\[
E = E_{\text{vb}} + B_c [J(J+1) - \frac{1}{2}K^2],
\]

(2.19)

where \( E_{\text{vb}} \) denotes the vibrational energy and \( B_c \) replacing \( 2 C \) in the \( K^2 \) term \(^{72}\) is the rotational constant for one of the in-plane axes. The vibrational energy \( E_{\text{vb}} \) is calculated from the harmonic frequencies that appear in the combination required. In the case of the \( S_1 \) state of benzene, use of the experimental fundamental frequencies \(^{72} v_i \) permits a calculation of the combination band origins with an accuracy of perhaps \( \pm 10 \text{ cm}^{-1} \), the combination band origin having an energy slightly different from the simple sum of fundamental frequencies, \(^{23} \) because of different combinations of anharmonic contributions.

The calculated vibration–rotation coupling in \( S_1 \) may depend somewhat on the exact placement of combination band origins, since differences in zeroth order energy levels enter as denominators in the perturbative expansions. The effect upon calculated spectral lines of this placement should be small if the calculation is “robust.” To test this robustness, a different energy randomly chosen between \( +10 \) and \( -10 \text{ cm}^{-1} \) was added to each dark zeroth order vibrational state in \( S_1 \). The \( S_1 \) eigenvector was recalculated using this set of randomly shifted dark state energies. Two further calculations with random shifts were performed. In each case, nonradiative linewidth, fluorescence quantum yield, and intensity at peak center were calculated for a given \( (J, K) \).

Vibrational matrix elements, including those found in Coriolis operators, typically contain factors such as \( \omega_i^{1/2} \) and \( \omega_j^{-1/2} \), where these \( \omega_i \)'s are the harmonic frequencies. Since we use experimental frequencies instead of harmonic ones, an error is made in these terms in the calculation, but it is much smaller than other error sources.

The individual matrix elements of the vibration–rotation Hamiltonian are obtained in the usual way after factoring into vibrational and rotational matrix elements of the relevant vibrational and rotational operators. Matrix elements of vibrational operators for one- and two-dimensional harmonic oscillators are well known. \(^{74} \) For matrix elements of rotational operators \( J_x \), \( J_y \), and \( J_z \), these latter are transformed to spherical tensor operators \( J_\alpha \), and \( J_0 \) and are evaluated in the standard way. \(^{65} \)

**D. Calculation of spectra**

1. **Modification of Eq. (2.11) for additional broadening**

In calculating the spectrum, we note that the line shape is a Voigt profile, namely, the convolution of a Gaussian instrumental shape and a Lorentzian one, the latter arising from fluorescence, nonradiative transitions, and pressure broadening. \(^{15} \) \( L \) in Eq. (2.11) now becomes

\[
L(v-v_0) = \frac{1}{\pi^{1/2} \Delta} \frac{\Gamma}{\pi} \int_{-\infty}^{\infty} \exp\left(-\frac{(u-v_0)^2}{\Delta^2/4} - \frac{(v-u)^2}{\Gamma^2/4}\right) du.
\]

(2.20)

The units of \( v \), \( \Gamma \), and \( \Delta \) are in megahertz, but now \( \Gamma \) has a contribution from pressure broadening \( \Delta_p \), in addition to the \( \Delta_{\text{nr}} \) and \( \Delta_f \) present in Eq. (2.11)

\[
\Gamma = \Delta_{\text{nr}} + \Delta_f + \Delta_p.
\]

(2.21)

Equation (2.20) can be rewritten in reduced form as

\[
L = \frac{1}{\pi^{1/2} \Delta} \frac{a}{\pi} \int_{-\infty}^{\infty} \exp\left(-\frac{y^2}{a^2}\right) dy,
\]

(2.22)

where

\[
x = 2(v-v_0)/\Delta, \quad a = \Gamma/\Delta.
\]

(2.23)

For \( \phi_f \), the quantum yield of the given \( J_K \) state in Eq. (2.9), one still uses Eq. (2.10), since in a fluorescence excitation experiment, the total emitted fluorescence is unchanged (see below). \( \Delta_f \) is 1.3 MHz and \( \Delta_p \) is about 15 MHz/Torr. \(^{15} \) With the 0.44 Torr used for the low \( J \) studies in Ref. 15, \( \Delta_p \) is 6.6 MHz. The high \( J \) spectrum, and also the low \( J \) spectrum, were obtained at 3.9 Torr, \(^{15} \) where the linewidth, apart from the \( \Delta_{\text{nr}} \) contribution, is about 60 MHz. \( \Delta \) in Eq. (2.23) is \( S/(\ln 2)^{1/2} \) MHz, corresponding to an instrumental Gaussian width at half-height of 5 MHz. \(^{15} \)

Several experiments suggest \(^{75} \) a mechanism for the pressure broadening and lead to Eq. (2.21). In experiments on a different spectral line, Wunsch et al. \(^{76} \) found that the total fluorescence of an initially excited ensemble of \( J_K \) states was pressure independent. (At longer times, the fluorescent lifetime was pressure dependent, presumably reflecting a collisional deactivation of the \( S_1 \) state as a whole.) Thus, at the times of interest here, the collisionally redistributed the electronic excitation of these fluorescence-emitting states among other fluorescing \( J_K \) states rather than quench them as a whole. However, the linewidth of an individual \( J_K \) state varies linearly with pressure. \(^{15,75} \) (The slope corresponds to a large, i.e., greater than gas kinetic, cross section. \(^{15,75} \) ) From these results on total fluorescence and on linewidths, it can be inferred \(^{76} \) that the collisional broadening of an initially excited \( J_K \) state is due to collisional conversion to other \( J_K \) states. As such, the appropriate modification of Eq. (2.11) is to include such pressure broadening via the term in Eq. (2.21), while Eqs. (2.8)–(2.10) remain unchanged.

2. **Rotational factor in Eq. (2.9)**

The rotational factor in Eq. (2.9) is \(^{41} \)

\[
|C_{\text{rot}}|^2 = C_0 M_0 R_0 + C_1 M_1 R_1 + C_2 M_2 R_2,
\]

(2.24)

where for the \( 4Q \) branch \( (\Delta J = \Delta K = 0 \) of a totally symmetric \( (A_J \rightarrow A_J) \) transition involved in exciting the \( 14^{12}_K \) line, the symmetric isotropic contribution \( C_0 M_0 R_0 \) has \( C_0 = 1/3 \), the symmetric anisotropic contribution \( C_2 M_2 R_2 \) has \( C_2 = 1/30 \) for the counter-circularly polarized light used in Ref. 15 and 2/15 for the parallel polarized light used in Ref. 12. \(^{51} \) \( C_1 \) is zero for these two polarization combina-
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5017

5

Cm

F

z

g

%0

J(J f' 1)

J(J+1)

FIG. 1. Calculated linewidths (squares) at low J, plotted vs J(J+1), corresponding to excitation of eigenstates dominantly |1412, J, K〉 with $K=0$. The experimental linewidths (circles) are included.

ions when the photons are identical in energy,$^51$ the $R_s$ are known rotational factors, dependent on $J$ and $K$, and the $M_s$ are electronic factors.$^51$ The relative values of $R_0$ and $R_2$ reduce further the contribution of the $C_2M_2R_2$ term in Eq. (2.24), typically to only a few percent of the $C_2M_2R_0$ term,$^72$ and it is ignored here.

III. RESULTS FOR 1412 S1 BAND

Throughout this section, the results are based on the data for $q<9$, where $q$ is the net number of vibrational quanta exchanged in proceeding from the 1412, $J, K$ light state to dark states in $S_1$.

A. Electronic matrix element

The electronic matrix element for IC was evaluated by matching the slope of the calculated widths of the spectral lines for $K=0$, as a function of $J(J+1)$, with the limiting slope at low J of the experimental $K=0$ plot of the total linewidth vs $J(J+1)$. The resulting factor was used in all subsequent calculations. In both the experimental and calculated plots, the nonradiative linewidth at $J=0$ was negligible. In particular, in Fig. 1 the plot of the calculated linewidths of the light state are given vs $J(J+1)$ for $K=0$ and $J=2, 6, 9, 12$ (cf. Sec. III B 1) with the experimental points superimposed. The slopes of calculated and experimental results at low J match when the electronic matrix element for IC is chosen to be $3.6 \times 10^5$ cm$^{-1}$. As noted previously, this value was used for simplicity in the calculations, regardless of whether $Q_{14}$ or $Q_{15}$ was the promoting mode. (For $J_K=6s$, about 60% to 65% of $\Delta_{nr}$ was calculated to be due to $Q_{14}$, given such an approximation.) The experimental and calculated intercepts in Fig. 1 are both very small (<2 and 1.6 MHz, respectively).

The material presented below is based on the above value for the electronic matrix element in IC. If more contributions to $\Delta_{nr}$ were used, arising from higher $q$ or higher order anharmonicities, e.g., the magnitude of the electronic factor needed for agreement of the low $J \Delta_{nr}$ vs $J(J+1)$ plot would be smaller.

B. Calculated linewidths $\Delta_{nr}$, quantum yields $\phi$, and peak areas $I_{JK}$

1. Low J

For purposes of calculating the fluorescence excitation spectrum, calculations were first made of the nonradiative linewidths $\Delta_{nr}$ for selected points. The values of $J=6$ and $J=12$ were selected as typical for low $J$, and the calculations were performed for different $K$, namely, $K=0, 1, 2, 4, 6$ for $J=6$; and $K=0, 2, 6, 12$ for $J=12$. The values $K=0$ and $K=0$ correspond to the absence and presence of parallel Coriolis coupling, respectively. The results for $\Delta_{nr}$ for the above $J_K$ states are given in Table I, based on coupling to dark $S_1$ states differing from the 1412 light state in up to nine vibrational quanta. Also listed are the coefficients $c_J$ of the light state in the normalized $S_1$ molecular eigenvector. In Fig. 2, the calculated linewidths $\Delta_{nr}$ of the $K>0$ states at low $J$ are plotted vs $K$ for $J=6$ and $J=12$, and compared with the values obtained from the interpolation formula (B1) in Appendix B. A comparison with Eq. (B1) is given in Table I for all points.

![Graph](image_url)

FIG. 2. Calculated linewidths at low J, plotted vs K for J=6 (circles) and for J=12 (squares). A comparison is given with the linewidths (solid lines) obtained using interpolation formula (B1).

---

TABLE I. Calculated nonradiative linewidth $\Delta_{nr}$, integrated line intensity $I_{JK}$, and the coefficient squared of the light state in the $S_1$ eigenvector for various low $J$ states.

<table>
<thead>
<tr>
<th>$J_K$</th>
<th>$\Delta_{nr}$ (MHz)</th>
<th>$I_{JK}$</th>
<th>$c_J^2$</th>
<th>$\Delta_{nr}$ (MHz) [Eq. (B1)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.6</td>
<td>0.72</td>
<td>1.00</td>
<td>1.6</td>
</tr>
<tr>
<td>2</td>
<td>3.6</td>
<td>2.7</td>
<td>1.00</td>
<td>1.6</td>
</tr>
<tr>
<td>6</td>
<td>17</td>
<td>2.9</td>
<td>0.99</td>
<td>17</td>
</tr>
<tr>
<td>61</td>
<td>26</td>
<td>1.7</td>
<td>0.99</td>
<td>28</td>
</tr>
<tr>
<td>62</td>
<td>52</td>
<td>0.78</td>
<td>0.98</td>
<td>53</td>
</tr>
<tr>
<td>64</td>
<td>150</td>
<td>0.28</td>
<td>0.94</td>
<td>140</td>
</tr>
<tr>
<td>66</td>
<td>300</td>
<td>0.15</td>
<td>0.90</td>
<td>280</td>
</tr>
<tr>
<td>90</td>
<td>33</td>
<td>1.2</td>
<td>0.98</td>
<td>24</td>
</tr>
<tr>
<td>120</td>
<td>58</td>
<td>1.8</td>
<td>0.97</td>
<td>58</td>
</tr>
<tr>
<td>122</td>
<td>95</td>
<td>0.76</td>
<td>0.96</td>
<td>94</td>
</tr>
<tr>
<td>126</td>
<td>330</td>
<td>0.23</td>
<td>0.89</td>
<td>320</td>
</tr>
<tr>
<td>1212</td>
<td>1100</td>
<td>0.05</td>
<td>0.74</td>
<td>1100</td>
</tr>
</tbody>
</table>

$I_{JK}$ denotes relative peak area (relative integrated line intensity) and is given by Eq. (2.9).
TABLE II. Calculated nonradiative linewidth $\Delta_{nr}$, integrated line intensity $I_{J,K}$, and the squared coefficient of the light state in the $S_1$ eigenvector for states with $J=42$, 36, and 30.$^a$

<table>
<thead>
<tr>
<th>$J,K$</th>
<th>$\Delta_{nr}$ (MHz) $\times 10^{-2}$</th>
<th>$I_{J,K}$</th>
<th>$\delta^2$</th>
<th>$\Delta_{nr}$ (MHz) $\times 10^{-2}$ [Eqs (B2)-(B3)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>4242</td>
<td>2.1</td>
<td>1.0</td>
<td>0.99</td>
<td>2.2</td>
</tr>
<tr>
<td>4241</td>
<td>5.8</td>
<td>0.24</td>
<td>0.96</td>
<td>6.4</td>
</tr>
<tr>
<td>4240</td>
<td>7.9</td>
<td>0.13</td>
<td>0.94</td>
<td>7.8</td>
</tr>
<tr>
<td>4239</td>
<td>14</td>
<td>0.07</td>
<td>0.90</td>
<td>13</td>
</tr>
<tr>
<td>4238</td>
<td>31</td>
<td>0.03</td>
<td>0.79</td>
<td>29</td>
</tr>
<tr>
<td>4237</td>
<td>53</td>
<td>0.01</td>
<td>0.68</td>
<td>53</td>
</tr>
<tr>
<td>3646</td>
<td>2.0</td>
<td>1.3</td>
<td>0.99</td>
<td>1.8</td>
</tr>
<tr>
<td>3635</td>
<td>4.4</td>
<td>0.34</td>
<td>0.95</td>
<td>4.6</td>
</tr>
<tr>
<td>3634</td>
<td>6.3</td>
<td>0.19</td>
<td>0.95</td>
<td>5.6</td>
</tr>
<tr>
<td>3632</td>
<td>9.5</td>
<td>0.11</td>
<td>0.93</td>
<td>9.4</td>
</tr>
<tr>
<td>3629</td>
<td>21</td>
<td>0.05</td>
<td>0.86</td>
<td>20</td>
</tr>
<tr>
<td>3626</td>
<td>33</td>
<td>0.02</td>
<td>0.80</td>
<td>36</td>
</tr>
<tr>
<td>3030</td>
<td>1.4</td>
<td>1.6</td>
<td>0.99</td>
<td>1.5</td>
</tr>
<tr>
<td>3029</td>
<td>2.6</td>
<td>0.54</td>
<td>0.98</td>
<td>3.2</td>
</tr>
<tr>
<td>3028</td>
<td>3.6</td>
<td>0.32</td>
<td>0.97</td>
<td>3.8</td>
</tr>
<tr>
<td>3026</td>
<td>7.4</td>
<td>0.15</td>
<td>0.95</td>
<td>6.1</td>
</tr>
<tr>
<td>3023</td>
<td>13</td>
<td>0.09</td>
<td>0.91</td>
<td>12</td>
</tr>
<tr>
<td>3020</td>
<td>22</td>
<td>0.04</td>
<td>0.86</td>
<td>22</td>
</tr>
<tr>
<td>3018</td>
<td>18</td>
<td>0.04</td>
<td>0.81</td>
<td>22</td>
</tr>
<tr>
<td>3017</td>
<td>17</td>
<td>0.05</td>
<td>0.82</td>
<td>22</td>
</tr>
<tr>
<td>3010</td>
<td>19</td>
<td>0.03</td>
<td>0.80</td>
<td>22</td>
</tr>
</tbody>
</table>

$^a$ $I_{J,K}$ denotes relative peak area (relative integrated line intensity) and is given by $\phi_J$ (2.9).

These $(J,K)$ lines in the spectrum were given quantum yields $\phi_J$ obtained from Eq. (2.10). A value of $\Delta_f=1.3$ MHz was used in all calculations.$^{15}$ Values of $I_{J,K}$ were then obtained from Eq. (2.9) by introducing the nuclear spin statistics$^{22-24}$ and Boltzmann factors. The resulting values of $\phi_J$ and $I_{J,K}$ are given in Table I.

2. High J

Calculations were made for $\Delta_{nr}$, $\phi_J$, and $I_{J,K}$: when $J=30$ for $K=30$, 29, 28, 26, 23, and 20; for $J_K=36$, 36, 36, 36, 36, and 36; and for $J_K=42$, 42, 42, 42, 42, 42, 42, 42, 42, and 42, these values being typical at high $J$. (Values of $K$ were selected such that $J-K=0$, 1, 2, 4, 7, and 10.) The results are given in Table II. The rotational temperature was 293 K. Calculations of $\Delta_{nr}$, $\phi_J$, and $I_{J,K}$ were also made when $J=30$, but for low $K$, namely, for $J_K=30$, 30, and 30, and are given in Table II.

In Fig. 3, the calculated nonradiative linewidths $\Delta_{nr}$ at high $J$ are plotted vs $(J-K)$ for $J=30$, 36, and 42. The solid curves are obtained from an interpolation formula in Appendix B. The results for $\Delta_{nr}$ (calc) for all points at high $J$ and $K$ are compared in Table II with those obtained from the interpolation formulas (B2) and (B3) in Appendix B. The states 30, 30, and 30 were not used in this interpolation.

C. Fluorescence excitation lines and spectra

The appearance of the Doppler-free two-photon spectra of the $14^112^2$ band$^{10,12,14-16}$ is qualitatively different for the two sets of experimental conditions low $J$ and high $J$. The prepared states, dominantly $|14^112^2,J,K\rangle$ in parentage, had $0<J<14$ in the data given at low $J^{12,14-16}$ while $J$ is typically 27 to 45 in the results at high $J^{22}$ The study was made at room temperature. The low $J$ and high $J$ cases are considered separately. These spectra occupy the 0 to $-60$ and $-100$ to $-270$ GHz (relative to the 0 line)$^{77}$ regions of the $0^Q$ branch of the fluorescence excitation spectrum, respectively. The several lines in the intervening region of $-60$ to $-100$ GHz remain to be assigned.

1. Low J

The line positions in the spectrum were calculated based on a symmetric top rigid rotor model in both the ground and excited electronic states, with a change in rotational constants $(B_{S0} - B_{S1})$ of 0.189 80$-$0.18 108 $=0.00872$ cm$^{-1}$. The rotational temperature assumed for all studies is 293 K, all experiments having been performed at room temperature.
The calculated spectral lines result from the convolution in Eq. (2.20). The value of $L$ in Eq. (2.20) when integrated over a $J_K$ line is unity, and so the integrated relative intensity of that line is given by $I_{J,K}$ in Eqs. (2.9) and (2.10). In the plots of the spectra, Eqs. (2.21)-(2.23) are used, in conjunction with Eqs. (2.8)-(2.10), with the $\Delta_r$ appropriate to the pressure employed.

The resulting calculated fluorescence excitation spectrum for low $J$ is given in Fig. 4, using the interpolation for $\Delta_r$, described in Appendix B, and from it, $\phi_J$ and $I_{J,K}$. For comparison, the same result is given, but for $q<6$, in Fig. 5. Both Figs. 4 and 5 correspond to an experimental pressure of 0.44 Torr, at which the linewidth contribution due to pressure broadening is about 6 MHz. In Fig. 6, the calculated spectrum at low $J$ for the higher pressure of 3.9 Torr is given, the contribution to the width due to pressure broadening now being about 60 MHz. The “bin” sizes used in generating the spectra, corresponding to those used in the experimental recording, are noted in Ref. 78.

In Fig. 7, a “stick spectrum” is given, namely, a plot of the integrated intensity of each line $I_{J,K}$ calculated from Eqs. (2.9) and (2.10). For comparison with the intensities, the rotational/spin statistics weighting factors for $J_K$ states with $0<J<15$ for $K=0$, and with $27<J<45$ for $K=J$, at a rotational temperature of 20 °C are shown in Fig. 8.

2. High $J$

The calculated spectrum for $J_K=27-45$ is given in Fig. 9, using a pressure of 3.9 Torr. This spectrum was based on a ($J,K$)-dependent fluorescence quantum yield obtained using the interpolation formulas (B2) and (B3) for $\Delta_{nr}$ in Appendix B, mentioned earlier. One interpolation formula (B2) is used for $J=K$ and one [Eq. (B3)] for $J\neq K$, since the transitions at $J=K$ are “one sided,” i.e., only a negative $\Delta K$ can occur, while for $J\neq K$, both positive and negative $\Delta K$ is possible. (At low $J$, when $K=0$, all transitions were “two sided.”) The stick spectrum for the relative integrated intensities $I_{J,K}$ of each line, based on Eqs. (2.9) and (2.10), is given in Fig. 10.
FIG. 9. The calculated fluorescence excitation spectrum for the red portion (−100 to 270 GHz) of the Q branch relevant for the high values of J at 293 K and a pressure of 3.9 Torr.

D. Results on particular aspects of the calculations

1. Number of Coriolis operators at low J and at high J

The contributions of paths containing different numbers of Coriolis operators (with the remaining anharmonic operators providing the exchange of vibrational quanta) were investigated at both low and at high J. For low J, the contributions to the nonradiative linewidth of paths containing zero (purely anharmonic) and one Coriolis operator are given in Table III for the JK=6,4 state. The same paths there have been categorized according to q, the number of vibrational quanta exchanged, and according to the perturbation order (H11) and type (parallel, perpendicular) of the Coriolis operator. All results are for q<9. The contributions of two-Coriolis paths to the nonradiative linewidth for the 64 state are given in Table IV. They contribute only about 15% of the total nonradiative linewidth.

The linewidth contains a small calculated contribution (∼0.4 MHz) from direct IC to S0 from the light state [14+1;6,4], i.e., without involving other S1 states. The contribution due to paths with only cubic anharmonic op-

*Paths may involve cubic anharmonic operators with and without a single parallel or perpendicular Coriolis operator. Values of Δnr are in megahertz.

q is the number of vibrational quanta exchanged.

† and ‡ represent paths with one Coriolis operator of the type indicated.

These values include q<3 as well.

FIG. 10. The calculated stick spectrum, i.e., the integrated line intensities IJK, for the red portion of the Q branch relevant for the high values of J at 293 K.


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TABLE III. Contributions to the nonradiative linewidth Δnr of purely anharmonic and of different types of Coriolis paths for JK=6,4.

<table>
<thead>
<tr>
<th>q</th>
<th>H30</th>
<th>Coriolis type</th>
<th>H21</th>
<th>H31</th>
<th>H41</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0.25</td>
<td>0.30</td>
<td>0.65</td>
<td>0.59</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.30</td>
<td>1.3</td>
<td>1.9</td>
<td>2.4</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.12</td>
<td>7.6</td>
<td>4.5</td>
<td>9.2</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>0.08</td>
<td>0.9</td>
<td>0.6</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0.06</td>
<td>15.7</td>
<td>4.6</td>
<td>9.3</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>0.04</td>
<td>10.1</td>
<td>2.3</td>
<td>4.2</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>0.03</td>
<td>8.0</td>
<td>1.7</td>
<td>3.1</td>
<td></td>
</tr>
</tbody>
</table>

Values of Δnr are given for different q and combinations (parallel, perpendicular) of Coriolis operators of different orders (H21, H31, H41). Values are in megahertz.

† and ‡ represent Coriolis operators of the type indicated. The first symbol represents the first Coriolis operator listed in the column heading and similarly for the second symbol. When the two Coriolis operators are different, their order of occurrence in a path is not implied by their order of listing, e.g., H2,H3, includes paths in which Hst occurs first.

A space is blank when the given combinations of operators do not occur in paths with the given value of q [cf. Eq. (2.18)].

By symmetry, the value for ‡ equals that for †. Their sum is listed under †, †.

TABLE IV. Contribution of paths with two Coriolis operators to the nonradiative linewidth for JK=6,4.

<table>
<thead>
<tr>
<th>q</th>
<th>Type</th>
<th>H30</th>
<th>H21</th>
<th>H31</th>
<th>H41</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0.02</td>
<td>0.04</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.11</td>
<td>0.17</td>
<td>0.07</td>
<td>0.07</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.36</td>
<td>0.23</td>
<td>0.17</td>
<td>0.18</td>
<td>0.09</td>
</tr>
<tr>
<td>6</td>
<td>0.10</td>
<td>0.06</td>
<td>0.09</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0.50</td>
<td>0.41</td>
<td>0.44</td>
<td>0.32</td>
<td>0.29</td>
</tr>
<tr>
<td>8</td>
<td>0.53</td>
<td>0.37</td>
<td>0.63</td>
<td>0.32</td>
<td>0.45</td>
</tr>
</tbody>
</table>

Values of Δnr are given for different q and combinations (parallel, perpendicular) of Coriolis operators of different orders (H21, H31, H41). Values are in megahertz.

† and ‡ represent Coriolis operators of the type indicated. The first symbol represents the first Coriolis operator listed in the column heading and similarly for the second symbol. When the two Coriolis operators are different, their order of occurrence in a path is not implied by their order of listing, e.g., H2,H3, includes paths in which Hst occurs first.

A space is blank when the given combinations of operators do not occur in paths with the given value of q [cf. Eq. (2.18)].

By symmetry, the value for ‡ equals that for †. Their sum is listed under †, †.
The utility of the path analysis in Tables IV and V, and that in a subsequent paper, depends on the absence of any major quantum interference between the various paths leading to the same dark $S_1$ state. Only in such a case is it meaningful to speak of contributions from the individual mechanistic paths. The nonradiative linewidth $\Delta_{nr}$ is then a sum of fractional linewidth contributions from individual paths. Specifically, $c_i$, the coefficient of the $i$th dark $S_1$ state in the $S_1$ eigenstate, is a sum over the paths or over classes of paths, labeled by $p$, leading to it from the light state $c_i = \sum_p c_{ip}$. Since the nonradiative linewidth is a sum over $i$ with contributions proportional to the square of the coupling matrix elements, we have

$$\Delta_{nr} = C \sum_{i,j} c_i^2 (FC)_{ij} = C \sum_{i,j} (c_i^2 p + \text{cross terms}) (FC)_{ij},$$

the cross terms being $c_i c_{ip'} p' \neq p$, $C$ being a constant. In Eq. (3.1), $(FC)_{ij}$ is the Franck-Condon factor for IC coupling from the $S_1$ dark state $i$ to the $S_0$ state $j$.

In Tables III and V, the sum of fractional contributions to the nonradiative linewidth from different paths is nearly identical to the total nonradiative linewidth for the $J_K=6_4$ (Table III) and $J_K=30_{26}$ (Table V) states. The sums are 149 MHz for $J_K=6_4$ and 699 MHz for $J_K=30_{26}$, compared with $\Delta_{nr}$ for these states of 150 and 706 MHz, respectively.

### 2. Number of vibrational quanta exchanged in $S_1$

To explore the relative contributions to the width $\Delta_{nr}$ arising from $S_1$ final dark states differing from the $14^1_{12}$ state by various $q$, the final dark states in $S_1$ differing in their vibrational principal quantum numbers (i.e., not counting $l$ substrates) within $\pm 20$ cm$^{-1}$ of $14^1_{12}$ were counted, a sufficient number of states being in this range to be indicative of the manifold of $S_1$ states as a whole. In the actual calculations of $\Delta_{nr}$, however, no such restriction of $S_1$ energies to $\pm 20$ cm$^{-1}$ was actually made. This count of states for the $J_K=6_4$ light state and their contribution to $\Delta_{nr}$ are given in Table VI, the states considered being those of ungerade parity since, as noted earlier, only they may couple with the $14^1_{12}$ zeroth order state of $b_{\gamma\delta}$ symmetry. There are (including $14^1_{12}$) 297 states which differ in their vibrational principal quantum numbers and are in the $\pm 20$ cm$^{-1}$ interval. Including $l$ substrates, the total density of vibrational band states of ungerade parity is about 85 per cm$^{-1}$. The calculations of $\Delta_{nr}$ in the previous sections were limited to $q$ equal to or less than nine, due in part to computer time, since the number of paths searched rises rapidly with $q$. To have included states with $q=10$ and $q=11$ using the present procedure would have taken an estimated ten- or 20-fold increase in central processing unit (CPU) time. In Table VI, the largest contributions to $\Delta_{nr}$ arise from $q=5$ and 6.

**Table V. Contributions to the nonradiative linewidth $\Delta_{nr}$ of paths containing different numbers and types of Coriolis operators for high $J$ for various $J_K$ states.**

<table>
<thead>
<tr>
<th>Path type</th>
<th>$30_{30}$</th>
<th>$30_{26}$</th>
<th>$30_{20}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.1</td>
<td>0.9</td>
<td>0.8</td>
</tr>
<tr>
<td>[1 ]</td>
<td>74</td>
<td>85</td>
<td>87</td>
</tr>
<tr>
<td>[2 ]</td>
<td>5.5</td>
<td>69</td>
<td>220</td>
</tr>
<tr>
<td>[3 ]</td>
<td>40</td>
<td>43</td>
<td>46</td>
</tr>
<tr>
<td>[4 ]</td>
<td>8.7</td>
<td>110</td>
<td>310</td>
</tr>
<tr>
<td>[5 ]</td>
<td>14</td>
<td>120</td>
<td>260</td>
</tr>
<tr>
<td>[6 ]</td>
<td>1.3</td>
<td>270</td>
<td>1300</td>
</tr>
</tbody>
</table>

*Values are in megahertz and have been rounded off to two significant figures. The results are for $q<9$.

\[a\] indicates paths with only cubic anharmonic coupling. \[1 \] and \[p \] represent paths with one Coriolis operator of the type indicated. The final four rows are for paths with the indicated combinations of two Coriolis operators.

\[b\] The first symbol represents the first Coriolis operator that acts in a path starting at the light state and proceeding to the dark background state in $S_1$.

**Table VI. The number of vibrational states $n_q$ differing in principal vibrational quantum numbers and contributions to $\Delta_{nr}$ of $S_1$ dark states within $\pm 20$ cm$^{-1}$ of the $J_K=6_4$ light state.**

<table>
<thead>
<tr>
<th>$q$</th>
<th>$n_q$</th>
<th>$\Delta_{nr}$</th>
<th>$q$</th>
<th>$n_q$</th>
<th>$\Delta_{nr}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0</td>
<td>5</td>
<td>8</td>
<td>9</td>
<td>1.6</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>9</td>
<td>3</td>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>10</td>
<td>9</td>
<td>19.0</td>
<td>31</td>
</tr>
<tr>
<td>5</td>
<td>9</td>
<td>11</td>
<td>4</td>
<td>27.7</td>
<td>12</td>
</tr>
<tr>
<td>6</td>
<td>25</td>
<td>13</td>
<td>7</td>
<td>34</td>
<td>14</td>
</tr>
<tr>
<td>7</td>
<td>34</td>
<td>13</td>
<td>8</td>
<td>38</td>
<td>4</td>
</tr>
</tbody>
</table>

*Band origins are within $\pm 20$ cm$^{-1}$ of the $14^1_{12}$ band origin. $n_q$ is listed as a function of number of vibrational quanta $q$ by which these bands differ from $14^1_{12}$. Values of $\Delta_{nr}$ are in megahertz and represent the contribution from these different sets of states.
TABLE VII. The effect of the shift in $S_1$ vibrational band origins upon calculated spectral properties for $J_K=6_0$, $6_1$, $6_4$.

<table>
<thead>
<tr>
<th>$J_K$</th>
<th>$\Delta_{nr}$ (MHz)</th>
<th>$I_{JK}$</th>
<th>$c_i^2$</th>
<th>$\epsilon_0$</th>
<th>$\epsilon_1$</th>
<th>$\epsilon_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$17$</td>
<td>$17$</td>
<td>$17$</td>
<td>$17$</td>
<td>$17$</td>
<td>$17$</td>
<td>$17$</td>
</tr>
<tr>
<td>$16$</td>
<td>$16$</td>
<td>$16$</td>
<td>$16$</td>
<td>$16$</td>
<td>$16$</td>
<td>$16$</td>
</tr>
<tr>
<td>$15$</td>
<td>$15$</td>
<td>$15$</td>
<td>$15$</td>
<td>$15$</td>
<td>$15$</td>
<td>$15$</td>
</tr>
</tbody>
</table>

$^a$The first of three values employs the unshifted set of vibrational band origins. The second and third values employ band origins obtained as described in the text.

IV. DISCUSSION OF RESULTS

A. A comparison of calculated and experimental fluorescence excitation spectra

We first note that experimental linewidths $\gamma$ measured spectroscopically agree with those measured from time-resolved data using $\gamma=1/2\pi\tau$, $\tau$ being the time for signal decay to 1/e of its initial intensity. Accordingly, it follows that the lines are homogeneously broadened. The present model of a discrete $S_1$ "eigenstate" in an $S_0$ continuum requires such homogeneity and is supported by the arguments given in Ref. 16 and amplified later in Sec. IV C.

1. Electronic matrix element for internal conversion

The plot of calculated linewidth $\gamma$ vs $J(J+1)$ when $K=0$, given in Fig. 1, is linear in $J(J+1)$. The experimental linewidth for the $K=0$ lines, also given in Fig. 1, is similarly linear in $J(J+1)$, but only for $J<10$. The magnitude of the electronic matrix element in IC required to match the experimental slope of linewidth vs $J(J+1)$ ($K=0$), $3.6\times10^4$ cm$^{-1}$, is in reasonable agreement with the $ab$ initio value of $\approx10^7$ cm$^{-1}$ estimated many years ago by Albrecht.

2. Low $J$

The experimental fluorescence excitation spectrum at low $J$ (0-14) displays few rotational lines, compared with the same region of the $9Q$ rotational branch for excitation below the channel three region. Examples of the latter are the $14^1$ band at an excess vibrational energy of $1570$ cm$^{-1}$ and the $14^1$ band at $2493$ cm$^{-1}$. The residual low $J$ lines in the $14^1$ spectra were all assigned by Neuser et al. as having $K=0$. These authors also implicated Coriolis coupling to dark states to explain their data.

The results at low $J$ in Table I for $\Delta_{nr}$ and $I_{JK}$ were calculated using up to and including two parallel Coriolis coupling operators and enough vibrational operators to yield a net exchange of up to and including nine vibrational quanta ($q<9$) in $S_1$. The results (Table I and Fig. 4) may be compared with the experimental finding at low $J$ that only the $K=0$ lines are observed. With parallel Coriolis coupling in the $S_1$ state, it is seen in Table I that the vibration–rotation coupling for $K=0$ is so extensive that the calculated nonradiative linewidths $\Delta_{nr}$ and fluorescence quantum yields $\phi_f$ tend to lead to "washed out" (broadened and weakened) spectral peaks with increasing $K$.

When $K=0$, the parallel rovibrational Coriolis coupling is absent and the pure anharmonic and perpendicular Coriolis coupling alone provides access to dark states in the $S_1$ manifold, as noted above, and as reflected in the proportionality of $\Delta_{nr}$ to $J(J+1)$ in Fig. 1. For $K=0$, the square of a perpendicular Coriolis matrix element is proportional to $J(J+1)$. The IC from those $K=0$ states to $S_0$ still competes successfully with fluorescence from the $14^1$ light state, a result evident from the low values of both the experimental $14^1$ and the calculated $\phi_f$ for these states. (It may also be noted that internal conversion at

E. Energy deposition in $S_0$

The modes considered active or inactive in IC were given earlier in Sec. II B. The percentage of vibrational energy residing initially in the dominant accepting modes in $S_0$ for various values of $J$ and $K$, calculated using Eq. (2.16), is listed in Table X.
these energies is reported to be comparable to or greater than the competing process of intersystem crossing to a triplet state.\textsuperscript{31} However, the calculated linewidths when $K=0$ are small enough, and the intensity maximum large enough, that the residual $K=0$ rotational lines are sharp and observable.

The square of the matrix element for parallel Coriolis coupling is proportional to $K^2$, so explaining the term for $\Delta_{nr}$ dependent quadratically on $K^2$ in Eq. (B1). The $J_K=0$ state has no Coriolis coupling to dark states in $S_1$, and the experimental nonradiative linewidth $\Delta_{nr}$ from this state, obtained from time-resolved data,\textsuperscript{16} was only $<2$ MHz, as noted earlier (Sec. III B 1). The present calculations give $\Delta_{nr}$ for the $0_0$ rotational state of 1.6 MHz. These values are one to several orders of magnitude smaller than typical widths for the other lines in Table I.

Our electronic matrix element, it will be recalled, was chosen to match the experimental $K=0$ linewidth dependence on $J(J+1)$. Since the intercept of that plot is negligible, the present calculated $\phi_f$ values for $K=0$ at various $J$'s should, and do, agree well with the experimental values at low $J$. Taking, thereby, $\Delta_{nr}$ from 0 to be approximately zero, an experimental $\phi_f$ for each $K=0$ state for various $J$'s can be extracted from the time-resolved data by taking the ratio of the lifetime for the $0_0$ state (or that for the lifetime of a state below the channel three region) to that for the $K=0$ states. In the present calculations, on the average $\phi_f\approx 10^{-2}$ for $K=0$ and $10^{-3}$ for $K>0$, as can be seen from the $\Delta_{nr}$'s in Table I. In an earlier study, the experimental vibrationally, but not rotationally resolved $\phi_f$ was about $10^{-3}$ at the energy of the 14\textsuperscript{14}12 band,\textsuperscript{14} and there the majority of rotational states had $K>0$.

In the calculated low $J$ spectrum in Fig. 4, the $K=0$ lines dominate, with an alternating intensity (J even, J odd) due to nuclear spin statistical weights. The present calculated and observed\textsuperscript{15} spectra are qualitatively similar. When $q<6$ was used in the calculation, the resulting spectrum (Fig. 5) contains small peaks with $K=1$ lying toward the origin of the corresponding stronger $K=0$ lines. The experimental spectrum at low $J$ does not contain these additional peaks. Thereby, the desirability of including several (up to and including nine) vibrational quanta exchanged in $S_1$ is clear. The experimental spectra rotational lines with $J_K=2_0, 4_0, 6_0$, and $8_0$ are the most intense, as are the interpolated calculated values.

With a rotational temperature of 293 K, the ground state weight factor appearing in Eq. (2.9) $|C_{rot}(J',K',J'',K'')|^2(2J'+1)f_{mec}(J'',K'')f_{Boltz}(J'',K'')$ becomes large for $J>10$, as seen in Fig. 8. In our calculations, the absence of $K>0$ lines is due to rapid parallel Coriolis coupling causing $\Delta_{nr}$ to become large, and not to some statistical Boltzmann effect of smaller rotational populations. The statistical factor, in fact, is greater for $K>0$ in this region.

3. High $J$

The results of the present calculations for $q<9$, given in Table II and in Figs. 9 and 10, are in agreement with the observation that the experimental fluorescence excitation spectrum at high $J$ ($J=27-45$) displays a $K=J$ structure.\textsuperscript{15} For the $K=J$ lines in both the calculated (Fig. 9) and the observed\textsuperscript{15} fluorescence excitation spectra, there is again an alternating intensity (J even, J odd) due to nuclear spin statistical weights, and the higher peaks for $J_K=33_3$ and $39_3$ are also in accordance with the statistical weights.\textsuperscript{52} The observed decrease in peak intensity of the $K=J$ lines for $J>40$ is attributable, on the basis of the present calculations, to the effect of Coriolis coupling, and only slightly (cf. Fig. 8) to the decrease with increasing $J$ of the ground state Boltzmann factor.\textsuperscript{52} The general structures of both the experimental and calculated spectra are similar. The overall picture is one of dominant parallel Coriolis coupling at low $J$ and perpendicular Coriolis coupling at high $J$.

\begin{table}[h]
\centering
\caption{The effect of the shift in $S_1$ vibrational band origins upon calculated spectral properties for $J_K=30_0$, 30_6, 30_0.\textsuperscript{a}}
\begin{tabular}{|c|c|c|c|}
\hline
$J_K$ & $\Delta_{nr}$ (MHz) & $I_{LK}$ & $c_f$ \\
\hline
$2_0$ & 3.6 & 33 & 58 \\
$3.7$ & 32 & 56 \\
$3.9$ & 34 & 58 \\
$2.7$ & 1.2 & 1.8 \\
$2.6$ & 1.2 & 1.9 \\
$2.5$ & 1.2 & 1.8 \\
$1$ & 0.98 & 0.97 \\
$1$ & 0.98 & 0.97 \\
\hline
$\textsuperscript{a}$Cf. footnote a of Table VII.
\end{tabular}
\end{table}

\begin{table}[h]
\centering
\caption{The percentage of vibrational energy deposited in normal modes for $S_0$ states quasienertial with the 14\textsuperscript{14}12 light state.}
\begin{tabular}{|c|c|c|c|c|}
\hline
Mode & $\varphi_6$ & $\varphi_4$ & $\varphi_3$ & Ref. 31b \\
\hline
$\varphi_1$ & 2.8 & 6.3 & 4.4 & 9.6 \\
$\varphi_2$ & 69.8 & 67.6 & 69.3 & 65.0 \\
$\varphi_3$ & 3.0 & 4.9 & 4.0 & 2.8 \\
$\varphi_4$ & 7.2 & 3.1 & 4.9 & 3.7 \\
$\varphi_5$ & 4.2 & 5.3 & 3.9 & 5.4 \\
$\varphi_6$ & 3.1 & 5.1 & 3.3 & 2.1 \\
\hline
\textsuperscript{a}See Ref. 25
\textsuperscript{b}For an initial energy in $S_1$ of 3317 cm\textsuperscript{-1}.
\end{tabular}
\end{table}
Returning to the example of $J=30$, the calculated rotational lines when $K=J=30$ yields the peak that is the sharpest and of the greatest intensity among the $30K$ lines (Table II). For $J=36$ and 42, the sharpest, most intense lines also occur for $K=J$. For $K<J$, the fluorescence quantum yield and intensity decrease with decreasing $K$, while the nonradiative linewidth increases (e.g., Table II). Accordingly, the calculated rotational lines for $K<J$ are considerably diminished in intensity and have broader linewidths (Table II) as $K$ decreases for a given $J$. Since the coupling matrix element for perpendicular coupling is proportional to $[J(J+1) - K(K+1)]^{1/2}$ (for $\Delta K=\pm 1$), that coupling becomes stronger with decreasing $K$ for a given value of $J$. Additionally, however, whereas at $K=0$ the parallel Coriolis coupling is totally absent, the perpendicular Coriolis coupling at $K=J$ is small, but still present in the minus sign term in the above matrix element.

The square of the perpendicular Coriolis matrix element, given above, is at large $J$ proportional, approximately, to $J(J-K)$, whereas the calculated results are linear in $J(J+1)$. This difference is due to paths containing two Coriolis operators, in particular, to paths with two perpendicular Coriolis operators. In the absence of the second Coriolis operator, the calculated linewidths and fluorescence quantum yields at high $J$ were not robust in that these observables became quite sensitive to shifts in vibronic band origins, in contrast with the behavior at low $J$. For the light states $|14^{1}1^{2}, J, K\rangle$ with $J_{K}=30_{30}, 30_{36}$, and $30_{42}$, use of a single Coriolis operator resulted in more than a factor of 2 discrepancy upon comparison of two linewidths for the same pair of $(J,K)$ and differing only in placement of $S_{2}$ vibronic band origins.

Formally, the order of perturbation theory of a given term in the vibration–rotation Hamiltonian is given by Eq. (2.17). In Eq. (2.17), the harmonic oscillator and rigid rotor energies are present in zeroth order. However, the values of the $J$ and $K$ dependent operators increase with $J$ and $K$, and so it is useful to reorder the terms in the vibration–rotation Hamiltonian into groups that are of the same order of magnitude. A path coupling light and dark states and containing two rotational operators will couple at low $J$ in a different order of magnitude from the coupling at high $J$. Thereby, Coriolis operators become more effective at high $J$, relative to cubic anharmonic operators. Because of the importance of extra Coriolis operators, seen in Table V, it is not surprising that the robustness of the calculation at high $J$, as measured by the effect of shifting $S_{1}$ vibronic band origins upon nonradiative linewidth in Table IX, is made more secure by including one additional Coriolis operator.

At low $J$, the “direct” coupling of out-of-plane modes to in-plane modes by a single perpendicular Coriolis operator is less important than the “indirect” coupling via a single parallel Coriolis operator typically followed by in-plane/out-of-plane cubic anharmonic coupling. At high $J$, the considerable importance of paths involving two perpendicular Coriolis operators in Table V shows that direct coupling via two perpendicular Coriolis operators contributes dominantly to the coupling mechanism of the light state to dark $S_{1}$ states with large FC factors for the $K=J$ states in Table II. For $K=J$ states, paths with either a single parallel or two parallel Coriolis operators provide the majority of the nonradiative linewidth in the $J=30$ system described in Table V.

2. Number $q$ of $S_{1}$ viborical quanta exchanged

In obtaining Tables I and II, the approximation was made of restricting the coupling of the light state to dark states in $S_{1}$ which differ in no more than nine vibronic quanta. The number of $S_{1}$ dark states reached increases.

B. Further aspects of the calculations

1. The number of Coriolis operators at low $J$ and at high $J$

The effect of including paths which contain a second Coriolis operator is different at low and at high values of $J$. At low $J$, for the light state $J_{K}=6_{4}$, the second Coriolis operator provides an additional coupling of only about one-sixth, as seen by comparing Tables III and IV. In contrast, at high $J$, as seen in Table V, 90% of the linewidth is due to paths containing two Coriolis operators, in particular, to paths with two perpendicular Coriolis operators. In the absence of the second Coriolis operator, the calculated linewidths and fluorescence quantum yields at high $J$ are seen in Table II, upon addition of 58 MHz (in a Voigt profile, the present Gaussian contribution to the overall pressure broadening contribution is very large (58 MHz). The calculated values for $J_{K}=30_{30}, 30_{36}$, and $30_{42}$, use of a single Coriolis operator resulted in more than a factor of 2 discrepancy upon comparison of two linewidths for the same pair of $(J,K)$ and differing only in placement of $S_{1}$ vibronic band origins.

Formally, the order of perturbation theory of a given term in the vibration–rotation Hamiltonian is given by Eq. (2.17). In Eq. (2.17), the harmonic oscillator and rigid rotor energies are present in zeroth order. However, the values of the $J$ and $K$ dependent operators increase with $J$ and $K$, and so it is useful to reorder the terms in the vibration–rotation Hamiltonian into groups that are of the same order of magnitude. A path coupling light and dark states and containing two rotational operators will couple at low $J$ in a different order of magnitude from the coupling at high $J$. Thereby, Coriolis operators become more effective at high $J$, relative to cubic anharmonic operators. Because of the importance of extra Coriolis operators, seen in Table V, it is not surprising that the robustness of the calculation at high $J$, as measured by the effect of shifting $S_{1}$ vibronic band origins upon nonradiative linewidth in Table IX, is made more secure by including one additional Coriolis operator.

At low $J$, the “direct” coupling of out-of-plane modes to in-plane modes by a single perpendicular Coriolis operator is less important than the “indirect” coupling via a single parallel Coriolis operator typically followed by in-plane/out-of-plane cubic anharmonic coupling. At high $J$, the considerable importance of paths involving two perpendicular Coriolis operators in Table V shows that direct coupling via two perpendicular Coriolis operators contributes dominantly to the coupling mechanism of the light state to dark $S_{1}$ states with large FC factors for the $K=J$ states in Table II. For $K=J$ states, paths with either a single parallel or two parallel Coriolis operators provide the majority of the nonradiative linewidth in the $J=30$ system described in Table V.

2. Number $q$ of $S_{1}$ viborical quanta exchanged

In obtaining Tables I and II, the approximation was made of restricting the coupling of the light state to dark states in $S_{1}$ which differ in no more than nine vibronic quanta. The number of $S_{1}$ dark states reached increases.
with the number of vibrational quanta exchanged up to some point \((q \sim 9)\), as in Table VI. However, beyond \(q = 6\), the effective coupling to each dark \(S_1\) state, as measured by the \(\Delta_{av}\) contribution arising from the coupling of that dark state to \(S_0\) states, decreases with the number of quanta exchanged \(q\), as seen in Table VI.

### 3. Random shifts of \(S_1\) vibrational origins

The majority of effective couplings to \(S_0\) (as measured by contributions to the nonradiative linewidth) is via dark states in \(S_1\) with large FC factors, states not necessarily close in energy to the light state. For these dark states, random shifts in energy denominators have a small effect on their matrix elements, since they are detuned from the light state by energies greater than the \(\pm 10\) cm\(^{-1}\) random shifts. Thereby, the overall sensitivity to uncertainties in the energies of the \(S_1\) dark states is expected to be small. From Tables VII and VIII, this small sensitivity is shown to be the case at low \(J\), with the nonradiative linewidth differing by at most several percent. At high \(J\), the sensitivity is greater, but still relatively small, with differences in nonradiative linewidth of at most 15% (cf. Table IX).

### 4. Neglect of anharmonic terms higher than \(H_0\)

The approximation was made of neglecting anharmonic terms higher than cubic. The coupling of light and dark states in \(S_1\) differing in several quanta would become more direct when higher order anharmonic terms such as quartic and quintic are included, fewer operators then being needed to exchange the desired number of quanta. However, the number of such paths is limited relative to the number of paths involving cubic anharmonicity alone, as can be seen using a simple path model described in a subsequent paper. Nevertheless, at some point, it would be very useful to include higher order anharmonicities for the \(S_1\) states in the calculation. They would provide additional pathways to the various \(S_1\) states. Such effects would also yield, as would the inclusion of terms with \(q > 9\), a somewhat smaller electronic matrix element for \(IC\), so as to match again the low \(J\) slope of the experimental linewidths at \(K = 0\).

### C. Statistical model

#### 1. Initial deposition of vibrational energy in \(S_0\)

In the initial distribution of vibrational energy in \(S_0\) states given in Table X, the most prominent accepting modes are seen to be out of plane, with mode \(Q_4\), of \(b_{2g}\) symmetry being particularly important. It was calculated that approximately 70% of the vibrational energy in the \(S_0\) states after IC resides initially in \(Q_4\), regardless of the rotational state. Out-of-plane modes \(Q_{16}\) and \(Q_{17}\) also receive an appreciable fraction of the excess energy.\(^{32-36}\) The in-plane modes \(Q_1\) (symmetric ring stretch) and \(Q_{14}\) (inducing mode) are also acceptors.

Out-of-plane modes were implicated in previous calculations as the dominant energy acceptors for internal conversion in benzene.\(^{32-36}\) Some of these results for an initial vibrational energy in \(S_1\) of 3317 cm\(^{-1}\) are listed in the last column of Table X. In this earlier model, mode \(Q_4\) is cited as accepting about 70% of the vibrational energy in \(IC\), in agreement with the present values, the present values being somewhat independent of \((J, K)\). The remaining major energy acceptors are the same as the present ones, namely, the six modes listed in Table X. In general, modes which differ the most between \(S_1\) and \(S_0\) will have the largest Franck-Condon factors, the difference either being in the coordinate position, or, as in \(Q_4\), where the equilibrium position is the same [only totally symmetric \((a_{1g})\) modes can have different equilibrium positions], in the vibrational frequency.

The presently calculated vibrational energy distribution in \(S_1\) can be compared with that assumed\(^{32-34}\) in a statistical model. The content of the light state in the \(S_1\) "eigenstate" is clearly so large that any statistical approximation should exclude it, i.e., one should not use an unconstrained statistical model. So we proceed as follows: The contributions to the \(S_1\) eigenvector from all dark states were used to calculate an average vibrational occupation number \(\bar{n}_k\) for mode \(Q_k\),

\[
\bar{n}_k = \frac{\sum_{i \neq s} C_i^2 n_{i,k}}{\sum_{i \neq s} C_i^2},
\]

(4.1)

where the sums are over rovibrational states labeled by \(i\), excluding \(s\) the light state. In Eq. (4.1), \(C_i\) is the coefficient of the \(i\)th RRHO state in the \(S_1\) eigenvector and \(n_{i,k}\) is the principal vibrational quantum number for mode \(Q_k\) in that zeroth order state in \(S_1\).

For a statistical distribution of energy, the occupation numbers are given by

\[
\bar{n}_k = \frac{1}{e^{\hbar \omega_k / kT} - 1},
\]

(4.2)

where \(T\) is an effective temperature for the vibrational degrees of freedom in \(S_1\). Thereby, in a statistical model, a plot of \(\ln (1 + 1/\bar{n}_k)\) vs \(\omega_k\) should be linear with a slope of \(\hbar/\kappa T\). This plot is given in Fig. 11 for the light state \(14^{11}1^2;6,4\) and corresponds to a "temperature" of 980 K.
An approximate linearity of the data points is obtained if one excludes modes \( Q_1 \) and \( Q_{14} \), which are excited in the zeroth order light state, and also excludes the CH modes. In this way, roughly, a constrained statistical distribution of vibrational energy exists for the value of \( J_K \) considered. \( Q_1 \) and \( Q_{14} \) were omitted from Fig. 11, since they are clearly nonstatistical. The high frequency CH modes have also been omitted, since their excitation is too small for their results to be significant. In Refs. 32–34, no constraint was employed, all modes being treated statistically.

2. Justification of the single eigenstate model

The results of the present calculation yielded a value of the coefficient \( c^2 \) in the \( S_1 \) eigenstate as 0.94, and high values for the other states (Tables I and II), so providing an a posteriori justification of the present model of a single \( S_1 \) eigenstate in a continuum of \( S_0 \) states. It is of interest to contrast this situation with a statistical model. In a statistical model, one would expect many \( c_i \)'s contributing, with approximately equal weight instead of having \( c^2=0.94 \). The absence of a statistical behavior of the coefficients \( c_i \) in the \( S_1 \) eigenstate is to some extent also reflected in the sparceness of states in \( S_1 \) (really two factors contribute to the behavior in \( S_1 \)—the density of states \( \rho \) in \( S_1 \) and the typical matrix element \( V_{eff} \) connecting them). There are about 85 ungerade states/cm\(^{-1} \) with the same \( K \), or if coupling to \( \Delta K=\pm 1 \) states is included, there are about 250 states cm\(^{-1} \). [The calculated width of the \( 64_s \) state is, incidentally, only 150 MHz (\( \approx 0.005 \) cm\(^{-1} \)) and so there is only about one \( S_1 \) state in this width.] From the nonstatistical behavior (in the present calculations), \( \rho V_{eff} \) must be substantially less than unity and so \( V_{eff} \) is less than 1/250 cm\(^{-1} \). What the present calculations do, in effect, is to provide, among other things, a rather detailed description of this "\( \rho V_{eff} \)" in the \( S_1 \) state.

There are a number of bands for which high resolution benzene spectra are available, in or near the channel three region, besides the \( 14^1 \) band, and it would be interesting to study those systems.

V. CONCLUSIONS

Fluorescence excitation spectra have been calculated corresponding to preparation of molecular eigenstates in the first excited electronic state (\( S_1 \)) of benzene and IC to \( S_0 \). The calculated fluorescence quantum yield, linewidth, and intensity of spectral lines are in broad agreement with the low \( J \) and high \( J \) data, in that only the \( K=0 \) lines survive IC in the former and only the \( K=J \) lines largely survive in the latter, as seen in Tables I and II and in Figs. 4 and 6.

What is particularly encouraging about the above calculations is that even though the mechanism for disappearance of the \( K\neq J \) lines at high \( J \) is different from that for the \( K=0 \) lines at low \( J \), the theory provides a unifying treatment for both. At low \( J \), the parallel Coriolis forces, associated with a finite \( K \), couple the initially excited in-plane modes to other in-plane modes which have, however, a significant cubic anharmonic coupling to out-of-plane modes. The latter enhance internal conversion to the \( S_0 \) state because of their large Franck-Condon factors. At high \( J \), instead, the perpendicular Coriolis terms, which increase individually as \( J(J-K) \) increases, cause a coupling of the in-plane modes to out-of-plane modes and so enhance the internal conversion. They cause the \( K\neq J \) lines to broaden significantly and also diminish in fluorescence intensity.

The Coriolis matrix elements at large \( J \) become large enough, comparable with the cubic anharmonic matrix elements, that paths with two perpendicular Coriolis operators become important as we have seen above. In contrast, the important paths at low \( J \) have mainly a single Coriolis operator. It is clear from a detailed comparison with the experimental data that the present calculations are in accord with them at low and at high \( J \), but that there are additional effects which require further examination. The calculated linewidths at high \( J \) with \( K=J \) are too high by roughly a factor of 2 and those of \( \Delta \alpha \) too high by a slightly larger factor; there may be experimentally some curvature in the \( \Delta \alpha \) vs \( J(J+1) \) plot for \( J>8 \) when \( K=0 \); and the several spectral lines in the region between the low \( J \) and the high \( J \) data (\( \approx 100 \) to \( \approx 60 \) GHz) remain to be analyzed. It will be interesting to see whether the inclusion of higher anharmonicities play a significant role in the first two of these effects. It would also be highly desirable to obtain low pressure measurements of the \( J_{K=J} \) lines at high \( J \), to remove some congestion in the spectrum, see whether or not there is any regularity in the widths of these lines, and perhaps document better the above trends.

According to the present calculations, the behavior is nonstatistical (cf. Sec. IV C). A picture in which a zeroth order light state \( 14^1 \) would be excited, relax to a statistical distribution in \( S_1 \), and then undergo an internal conversion to \( S_0 \) is not a valid time-dependent interpretation of the spectroscopic observations, according to these calculations. Instead, the large values of \( c_i^2 \) in Tables I and II suggest instead a model in which a slightly perturbed \( K \) state in \( S_1 \) behaves as a "discrete state" in a "continuum" of states of \( S_0 \). Because of the high \( c_i^2 \) values, \( K \) is still a relatively good quantum number in describing the \( J_{K=0} \) states at low \( J \) and the \( J_{K=J} \) states at high \( J \). Experimental evidence against a statistical model was noted earlier.

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A. Helman and R. A. Marcus: Fluorescence excitation spectra. II
APPENDIX A: SOME RELEVANT FORCE AND OTHER COUPLING CONSTANTS—EVALUATION OF OVERLAP INTEGRALS

The cubic force constants used are taken from an ab initio force field for the ground state benzene. We have obtained from it the cubic force constants that involve only totally symmetric \((\sigma_{ij})\) linear combinations of three vibrational operators, of which there are 237 independent values. In the current absence of an excited state \(S_1\) cubic force field, the ground state \((\sigma_{ij})\) values were used, instead, for the cubic anharmonic constants.

Coriolis coupling constants were computed from the \(L\) matrix obtained using the quadratic force field solution of Ref. 86. The ground electronic state values obtained from a normal mode analysis were assumed for calculating the present set of Coriolis coefficients \(c_{ij}^{(k)}\). Inertial derivatives and higher order coefficients of the inverse inertia tensor were computed using the values \(r_{\text{CH}} = 1.084 \text{ Å}\) and \(r_{\text{CC}} = 1.397 \text{ Å}\) for the excited state carbon–hydrogen and carbon–carbon equilibrium bond lengths, respectively.

Ten of the 20 modes in benzene are nondegenerate. For them, standard formulas are available for computing their respective overlap integrals.\(^7\) Of these ten modes, two modes \(Q_1\) and \(Q_2\) are totally symmetric \((\sigma_{ij})\). For them, the relevant formulas are for displaced and distorted oscillators, since a net displacement of one parabolic well relative to the other is possible only along a totally symmetric coordinate. We have used the reported experimental values of \(\Delta Q_1 = 0.034 \text{ Å}\) and \(\Delta Q_2 = 0.01 \text{ Å}\).\(^8\) The value for \(\Delta Q_1\) reproduces the deep minimum in overlap for \(\{1|1\}\) which is predicted both from theoretical considerations,\(^9\) and observed in the \(v_1\) progressions of vibrationally resolved spectra.\(^9,91\) The remaining eight nondegenerate modes are only distorted.

For the remaining ten doubly degenerate modes, which may be distorted, but not displaced (since none of them are totally symmetric), we calculate overlap integrals using standard formulas for distorted, undisplaced two-dimensional harmonic oscillators.\(^5,5,92-94\)

APPENDIX B: INTERPOLATION TO OBTAIN SPECTRA

A principal aim of the present paper was to see whether at low \(J\), only the \(K=0\) lines, and whether at high \(J\), only the \(K=J\) lines effectively survive an IC competition and appear in the fluorescence excitation spectra. Figures 4–7 and 9–10 were obtained by interpolating the results in Tables I and II. The approximate interpolation formulas assumed for \(\Delta_{nr}\) are given below. From the value of \(\Delta_{nr}\) and \(\Delta_f\) (the latter taken to be the typical value of \(\Delta_f = 1.3 \text{ MHz}\) at lower energies), \(\phi_f\) can be calculated using Eq. (2.10), and from this \(\phi_f\), the relative values of \(I_{J,K}\) can also be obtained using Eq. (2.9). In this Appendix, all energies are in megahertz.

1. Low \(J\).

At low \(J\), we assume the nonradiative linewidths are fit well by including linear and quadratic terms in the \(J\) and \(K\) quantum numbers

\[
\Delta_{nr}(J,K) = 1.6 + aJ + bK + cJ^2 + dK^2, \quad (B1)
\]

the small value of 1.6 MHz being the \(\Delta_{nr}\) calculated for the \(J_K=0\) line. The coefficients \(a\) and \(c\) are first determined by a least squares fit for the \(K=0\) nonradiative linewidths. \(b\) and \(d\) are then found by a least squares fit of the remaining linewidths. For the low \(J\) spectrum with \(q<9\), \(a\), \(b\), \(c\), and \(d\) respectively, 0.346, 4.96, 0.361, and 6.61, the number of decimals definitely not indicating the accuracy or precision. The corresponding values for the low \(J\) spectrum with \(q<6\) are 0.414, 3.57, 0.329, and 4.20, respectively. The inclusion of terms quadratic in rotational quantum numbers corresponds to the inclusion of a single Coriolis operator at low \(J\), since the nonradiative rate scales quadratically with the rotational coupling matrix element. The fit of Eq. (B1) to the calculated \(\Delta_{nr}\)'s is seen in Table I and Fig. 2.

2. High \(J\).

At high \(J\), it is observed that when \(K=J\), the calculated nonradiative linewidths are small, the dominant two perpendicular Coriolis operator paths in \(S_1\) having small rotational matrix elements. Thereby, for \(K=J\), the nonradiative linewidth is approximated by a constant term and a term quadratic in \(J\), namely,

\[
\Delta_{nr}(J,K=J) = a_1 + b_1J^2 \quad (K=J). \quad (B2)
\]

A least squares fit to the calculated nonradiative linewidths yields \(a_1 = 71.6\) and \(b_1 = 0.0833\). Because the changes of \(K\) at \(J=K\) are "one sided," a different interpolation formula is used for \(K=J\) and for \(K<J\).

When \(K<J\), \(\Delta_{nr}\) is seen, at a given value of \(J\), to increase roughly as \((J-K)^2\), as in Fig. 3. As \(K\) approaches \(J\), the intercept of these \(K<J\) points is nonzero and scales as \(J^2\). Finally, for a given value of \((J-K)\), the nonradiative linewidth changes roughly linearly in \(J^2\). These observations suggest the functional form

\[
\Delta_{nr}(J,K) = aJ^2 + (b + cJ^2)(J-K)^2 \quad (K<J). \quad (B3)
\]

The coefficients \(a\), \(b\), and \(c\) are determined by a least squares fit of the \(K<J\) nonradiative linewidths (15 states were used) at high \(J\), except for the states \(J_K=300, 301, \) and \(304\), to Eq. (B3). For the high \(J\) spectrum with \(q<9\), \(a\), \(b\), and \(c\) are, respectively, 0.333, −10.12, and 0.0325. The fit of Eq. (B3) to the \(\Delta_{nr}\)'s is seen in Fig. 3 and the fits of Eqs. (B2) and (B3) are seen in Table II.

The Wilson (W) system numbers normal modes according to their irreducible representations. Mode $Q_{14}$ is an in-plane ring distortion of irreducible representation, since only then is the two photon absorption transition matrix element nonzero by symmetry arguments. By direct enumeration, the only states satisfying these criteria within 10 cm$^{-1}$ of the excitation wavelength belong to the 141$^2$ vibronic band.

The isotopomer $^{13}$C$_6$H$_6$ is assumed for calculation of nuclear statistical weights.

Since literature values of $S_1$ vibrational frequencies are reported to the nearest wave number, vibrational energies of RRHO states, being the sums of such frequencies, will only occur in clusters separated by 1 cm$^{-1}$ intervals. Various ways of randomly assigning states to lie in a 0.03 cm$^{-1}$ interval can be used.

Upon comparison of $c_i$ coefficients for a particular dark $S_1$ state, but with different $J$ values, e.g., $J_{0}$ and $J_{2}$, their ratio, as $c_i(J_{0})/c_i(J_{2})$, is somewhat independent of $c_i$ of state $i$. Therefore an average value for this ratio is assumed and is then used to set the cut-off criterion for that $J$ value.

The sum of the fundamentals $0_{01}+20_{02}$ is 3416 cm$^{-1}$, which differs from the energy of the 141$^2$ state (3412 cm$^{-1}$) because the anharmonicity makes a different contribution to these two quantities.

For the indirect coupling of light and dark states, obtained as a sum of such frequencies, will only occur in clusters separated by 1 cm$^{-1}$ intervals. Various ways of randomly assigning states to lie in a 0.03 cm$^{-1}$ interval can be used.

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\( \frac{C_o - B_o}{2} \), and so \((C_o - B_o)K^2\) becomes the term containing \(K^2\) in Eq. (2.19).

74 H. J. Neusser (private communication).
76 The range over which spectral lines have been calculated corresponds to \(J<15\) when \(K=0\).
77 We are indebted to Dr. E. Riedle for sending us copies of the experimental spectra. We have employed the bin sizes used there. In making our spectral plots, the "Voigt integral" in Eq. (2.23) was subdivided into values over these bin sizes. A "bin" size of 3 MHz was used, thereby, in generating the spectra in Figs. 4 and 5 at the low pressure of 0.44 Torr, while a bin size of 13 MHz was used for Fig. 6 at the higher pressure of 3.9 Torr and for Fig. 9 at the same pressure.
78 The coupling to dark states in \(S_1\) along a path to the final \(S_1\) dark states is not restricted to a \(\pm 20\) cm\(^{-1}\) window.
79 For a fixed cut-off value of the evaluation function, use of the rotational operator \(\mu_{\text{rot}}/\hbar\) yields fewer accepted coupling paths via IC, due to the inverse moment of inertia in the coupling operator.
81 Using a rotational temperature of 293 K, the Boltzmann factor may account for roughly a 30% decrease in line intensity for \(J>40\), compared to \(J=30\), which is insufficient to account for the observed decrease, the latter being due mainly to the increase of \(\Delta u_r\).
82 Reference 60, Chap. VII.
83 Reference 60, Chap. VII.
88 Normal mode \(Q_1\) is dominantly a ring breathing mode, while \(Q_2\) is dominantly a carbon-hydrogen stretch mode. Of these two modes, \(Q_1\) is much more important in vibration-rotation coupling and IC at the onset of channel three, since the \(v_2\) fundamental lies above 3000 cm\(^{-1}\).