Rotational branching ratios at low photoelectron energies in resonant enhanced multiphoton ionization of NO

H. Rudolph and V. McKoy
Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125

S. N. Dixit
Lawrence Livermore National Laboratory, L-401, P.O. Box 808, Livermore, California 94550

(Received 13 July 1988; accepted 18 November 1988)

We report calculated rotational branching ratios for very low energy (50 meV) photoelectrons resulting from (1 + 1′) resonant enhanced multiphoton ionization (REMPI) via the $J_i = 1/2$, 3/2, 5/2, and 7/2 levels of the P_{11} branch of the $A\,^2\Sigma^+ (3s\sigma)$ state of NO. Even angular momentum transfer ($\Delta N \equiv N_+ - N_i$) peaks are dominant in these rotational distributions, in agreement with the selection rule $\Delta N + l =$ odd. Angular momentum coupling in the photoelectron wave function arising from the molecular ion potential leads to smaller but appreciable $\Delta N =$ odd peaks. The calculated $\Delta N = 0$ to $\Delta N = +2$ peak ratios show the same strong decrease when J_i increases from 1/2 to 3/2 as seen in the experimental zero-kinetic-energy (ZEKE) photoelectron spectra [Sander *et al.*, Phys. Rev. A **36**, 4543 (1987)], but do not show the rapid die-off of the $\Delta N \neq 0$ peaks for higher J_i observed experimentally. The calculated trend in the $\Delta N = +2$ vs $\Delta N = 0$ peaks could be understood on the basis of simple angular momentum transfer arguments. These same arguments indicate that this trend in the $\Delta N = 0$ and +2 peaks with increasing angular momentum is not generally expected in other branches. Spectra via the $R_{21}(J)$ branch are presented to support this assertion. We also present photoelectron angular distributions which show a strong dependence on ΔN reflecting the changing composition of the photoelectron wave function.

I. INTRODUCTION

In recent years resonant enhanced multiphoton ionization (REMPI)-photoelectron spectroscopy (PES) has seen a substantial improvement in photoelectron kinetic energy resolution. Conventional time-of-flight (TOF) methods for PES have been sufficiently refined to provide rotationally resolved spectra for small molecules.[1–5] Due to the small rotational constants, studies in heavier molecules such as NO have focused on high-J levels of the ion. Recently, Müller-Dethlefs *et al.* have developed a novel method of zero-kinetic-energy (ZEKE) photoelectron spectroscopy.[6,7] This method employs photoionization under field-free conditions and application of a delayed pulse extraction field.[6,7] The technique, facilitated by steradiancy, yields a resolution of 1–2 cm^{-1} in threshold PES. In contrast, the TOF-PES studies at low energies by Allendorf *et al.*[5] achieve a resolution of 3–4 meV around an energy of 180 meV. Using this latter technique, Allendorf *et al.*[5] have recently reported photoelectron angular distributions for rotationally resolved PES of NO, a significant step towards the "complete" characterization of the photoionization process.

A common feature in these rotationally resolved REMPI-PES studies of NO has been the deviations of the branching ratios from values expected on the basis of an atomic-like model.[2,4,7] For example, ionization out of the $A\,^2\Sigma^+ (3s\sigma)$ state showed a $\Delta N = 1$ peak[5,7] ($\Delta N \equiv N_+ - N_i$, where N_+ and N_i denote the angular momentum quantum numbers, exclusive of spin, of the ion and resonant intermediate state, respectively). On the basis of the selection rule $\Delta N + l =$ odd,[8,9] the presence of this peak implies photoelectron ejection into the even l's of the continuum, i.e., $3s\sigma \rightarrow ks,kd$, etc.. This is inconsistent with an atomic-like view of the process which would predict ionization primarily into the p continuum. Explicit calculations of these rotational distributions for ionization out of both the $A\,^2\Sigma^+ (3s\sigma)$ and the $D\,^2\Sigma^+ (3p\sigma)$ states[9,16] quantitatively confirm this non-atomic-like behavior observed for high J values. The ZEKE-PES experiments of Sander *et al.*,[6,7] carried out through low N_i levels of the $A\,^2\Sigma^+$ state of NO, also display these non-atomic-like rotational branching ratios. For the $P_{11}(J)$ ($J = 3/2$–$7/2$) branch the $\Delta N = 0$ peak is, as expected, dominant. For $\Delta N \neq 0$, the even ΔN peaks are stronger than those for ΔN odd, in agreement with the $\Delta N =$ even propensity rule. However, the $\Delta N \neq 0$ peaks die off rapidly with increasing J of the resonant $A\,^2\Sigma^+$ state. This dynamically interesting behavior is in contrast to the observed branching ratios for ionization via the high J levels.[2,4,5]

In the present paper we report calculated rotational branching ratios for very low energy (50 meV) photoelectrons resulting from (1 + 1′) REMPI via these same low J levels of the P_{11} branch of the $A\,^2\Sigma^+$ state of NO. The main objective of these studies is to provide insight into the underlying reasons for the difference in the observed branching ratios for the high and low J levels. Although these calculated rotational branching ratios agree well with the observed

 0021-9606/89/052570-05$02.10

ZEKE values for $N_i = 0$ and 1, they do not show the rapid die off of the $\Delta N \neq 0$ peaks for higher N_i seen experimentally. It is, in principle, possible that non-Born–Oppenheimer behavior could influence these ZEKE spectra. However, the agreement between the calculated and measured ZEKE spectra for $N_i = 0$ and 1, suggests that these low-energy studies reproduce some of the essential dynamics of the ZEKE experiments. Furthermore, the calculated trends in $\Delta N = 2$ vs the $\Delta N = 0$ peaks could be understood on the basis of simple angular momentum transfer considerations. The validity of these arguments is further supported by the behavior of the branching ratios for REMPI via the $R_{21}(J)$ branch. To provide additional insight into the dynamics of the state-specific processes and for possible comparison with measurements we also present photoelectron angular distributions for ionization via the $P_{11}(J)$ branch.

II. THEORY

The framework for our analysis of REMPI processes has been described in detail elsewhere.[11] The $(1+1')$ REMPI process can be thought of as a one-photon excitation from an initially unaligned (all M_J levels equally populated) ground state ($X\,^2\Pi$) to an aligned resonant intermediate state ($A\,^2\Sigma^+$) followed by a one-photon ionization out of this state:

$$\mathrm{NO}\ X\,^2\Pi(v''=0,J'') \xrightarrow{h\nu} \mathrm{NO}^*\ A\,^2\Sigma^+(v'=0,J',N') \xrightarrow{h\nu'} \mathrm{NO}^+\ X\,^1\Sigma^+(v_+=0,J_+=N_+) + e^-(\mathbf{k}). \quad (1)$$

Each M_J level is treated as an independent ionization channel, in the absence of M_J mixing terms (collision-free conditions, etc.). The alignment of the resonant intermediate state is then determined using lowest-order perturbation theory for these weak field excitations. For a single photon $X\,^2\Pi \rightarrow A\,^2\Sigma^+$ transition, the relative population $\rho_{ii}(M_J)$ is determined by the 3-j coefficient through[12,13]

$$\rho_{ii}(M_J) \propto \begin{pmatrix} J' & 1 & J'' \\ M_{J'} & 0 & -M_{J'} \end{pmatrix}^2 A, \quad (2)$$

where J' and J'' are the rotational quantum number of the $A\,^2\Sigma^+$ and the $X\,^2\Pi$ states, respectively. $M_{J'}$ is the corresponding projection of J' on the z axis. The constant A is the one-photon line strength as given by Earls.[14] The relative values of ρ_{ii} do not depend on the line strengths for pure rotational branches. The total photoionization probability, $P(J',N',J'',N'',N_+)$, is given by an incoherent sum over the individual M_J levels' $\Gamma_i(J',N',N_+)$, weighted with the corresponding relative populations ρ_{ii}

$$P(J',N',J'',N'',N_+) = \sum_i \rho_{ii}\Gamma_i(J',N',N_+). \quad (3)$$

In Eq. (3) $\Gamma_i(J',N',N_+)$ is proportional to $\langle f|\mu|i\rangle^2$, the square of the dipole matrix element between the final continuum state $|f\rangle$, and the resonant intermediate state $|i\rangle$. Following Eq. (6) of Ref. 9, this matrix element can be written as ($\Lambda_i = \Lambda_+ = 0$)

$$\langle f|\mu|i\rangle = \sum_{N_t,\zeta} R(\zeta,N_t) \sum_{\mu} r_{fi}^{l\mu\mu}(-1)^{\mu} \times \begin{pmatrix} N_+ & N_i & N_t \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} N_t & 1 & l \\ 0 & \mu & -\mu \end{pmatrix}, \quad (4)$$

where N_+, N_i are the angular momentum of the ion and the resonant intermediate state (exclusive spin), respectively, N_t is the angular momentum transfer, l is the partial wave of the photoelectron orbital, and μ is its magnetic quantum number ($\mu = 0$ for the σ channel and $\mu = \pm 1$ for the π channels). $R(\zeta)$ represent products of 3-j coefficients and other angular momentum factors (see Refs. 9 and 11 for further details). The one-electron dipole matrix element $r_{fi}^{l\mu\mu}$ between the orbital of the resonant state and partial wave l of the photoelectron wave function, is defined by Eq. (13) of Ref. 9.

Using the properties of 3-j symbols[15] and the symmetry relationship $r_{fi}^{l\mu\mu} = r_{fi}^{l-\mu-\mu}$, it can be shown that the summation over μ in Eq. (4) vanishes unless $N_t + N_i + N_+ =$ even and $N_t + l =$ odd. These conditions lead to the selection rule[8]

$$N_+ - N_i + l \equiv \Delta N + l = \text{odd}. \quad (5)$$

This selection rule is independent of the excitation scheme to the intermediate state, and it is therefore applicable to any $(n+1)$ REMPI process with a final Σ–Σ transition.[8] The $3s\sigma$ Rydberg character of the $A\,^2\Sigma^+$ state of NO leads to a dominance of odd partial waves in the continuum (see later) and hence to a propensity rule of $\Delta N =$ even for the REMPI via the $A\,^2\Sigma^+$ state. This predicted propensity rule has been seen to be valid both experimentally and theoretically.[2,4,9,13]

For the $A\,^2\Sigma^+$ state we use a SCF wave function obtained using an extensive Gaussian basis set, described elsewhere.[12] This basis contains diffuse functions to ensure the correct behavior of the tail region of the 6σ orbital. A single center expansion of the 6σ orbital of NO about the center of mass has the following partial wave components: 94.0% s, 0.2% p, 5.5% d, and 0.1% f, in agreement with previous calculations by Kaufmann *et al.*[16] The photoelectron wave functions were obtained using the iterative Schwinger method[17,18] in the frozen-core approximation and retaining up to $l = 6$ in the partial wave expansion of the photoelectron wave function. All matrix elements were determined at $R_e(A\,^2\Sigma^+) = 2.0095$ bohr.[19] To model the ZEKE spectra we used a photoelectron energy of 50 meV. At this kinetic energy we do not expect any serious breakdown of the fixed-nuclei approximation for these rotational studies. The cross sections were also seen to be relatively insensitive to changes in kinetic energy in this region. The partial wave decomposition of the photoelectron matrix element ($|r_{fi}^{l\mu\mu}|$) for the $k\sigma$ channel is (normalized to the value of the p wave in the $k\pi$ channel): 0.1512, 0.2522, 0.2145, 0.3273, and 0.0069 for $l = 0,4$, respectively, and for the $k\pi$ channel: 1.0000, 0.0373, 0.4927, and 0.0094 for $l = 1,4$, respectively. The $l = 1$ channel is seen to be dominant, as anticipated on the basis of the bound state's high s character. The even-l waves, however, contribute significantly to these matrix elements. The rotationally unresolved cross sections are $\sigma_\sigma = 0.316$ Mb and

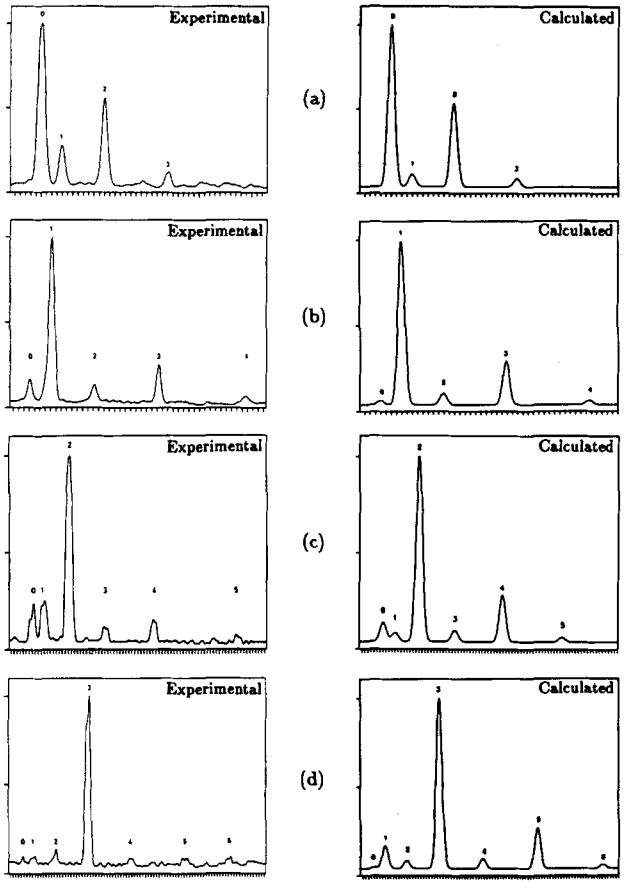

FIG. 1. (a) Experimental (Ref. 7) and calculated photoelectron spectra for REMPI via the P_{11} (3/2) branch of the 0–0 band of the $X\,^2\Pi$–$A\,^2\Sigma^+$ transition, $J_A = 1/2$, $N_A = 0$. The value of N_+ is shown above each peak; (b) same as (a), but via the P_{11} (5/2) branch, $J_A = 3/2$, $N_A = 1$; (c) same as (a), but via the P_{11} (7/2) branch, $J_A = 5/2$, $N_A = 2$; (d) same as (a), but via the P_{11} (9/2) branch, $J_A = 7/2$, $N_A = 3$.

$\sigma_\pi = 0.819$ Mb with a total cross section of $\sigma_{\text{tot}} = 1.135$ Mb (1Mb $= 10^{-18}$ cm^2), similar to earlier results at higher energies.[9]

III. RESULTS

In Fig. 1, we compare the ZEKE spectra of Sander *et al.*[7] for (1 + 1′) REMPI via the P_{11} (J) ($J = 3/2,5/2,7/2,9/2$) branches with our calculated spectra at a photoelectron kinetic energy of 50 meV. The calculated branching ratios have been normalized to the most intense peak ($\Delta N = 0$) and folded with a Gaussian detector function (FWHM = 1.0 meV), with a constant background signal added for experimental comparison. The position of the lines are calculated using molecular constant for the $A\,^2\Sigma^+$ state of NO from Ref. 19. The dominance of even ΔN peaks in these spectra reflects the strong contribution of odd partial waves to the photoelectron wave function. The nontrivial magnitudes of the odd ΔN peaks are a consequence of the nonspherical character of the molecular ion potential which leads to strong coupling of the partial waves of the photoelectron wave function.[9,10,12,13]

The agreement between the experimental and calculated PES of Figs. 1(a)–1(b) for ionization via the P_{11} (3/2) and P_{11} (5/2) branch, respectively, is remarkably good. One of the more striking features in the comparison of the spectra for $J_i = J_A = 1/2$ and $J_i = J_A = 3/2$ is the decrease in the relative intensity of the $\Delta N = 0$ to 2 peaks. This behavior can be understood in terms of angular momentum constraints imposed by Eqs. (4) and (5). In the case of the P_{11} (3/2) branch where $N_i = 0$, the only partial wave that can contribute to the $\Delta N = 0$ peak is $l = 1$ due to the requirement $N_+ = N_i = N_t = 0$. The $\Delta N = 0$ signal for the P_{11} (3/2) line is therefore a direct measure of the strength of the p

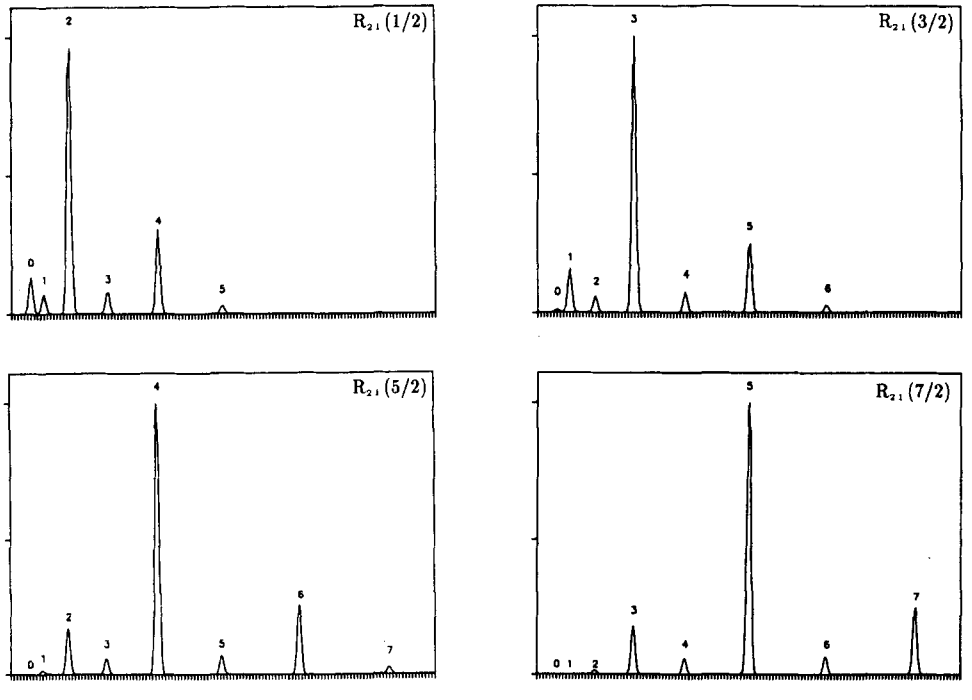

FIG. 2. Calculated photoelectron spectra for REMPI via the R_{21} (J) branches, $J = 1/2 - 7/2$, of the 0–0 band of the $X\,^2\Pi$–$A\,^2\Sigma^+$ transition. The value of N_+ is shown above each peak. $J_A = J_x + 1$, $N_A = J_A + 1/2$.

wave. Correspondingly, the value of the β_2 coefficient in the photoelectron angular distributions would be 2. All higher β coefficients must be zero for the $J_i = J_A = 1/2$ state. However, for the $P_{11}(5/2)$ line both $l = 1$ and 3 partial waves contribute to the $\Delta N = 0$ peak. Similarly, the $\Delta N = +2$ signals for these $P_{11}(3/2)$ and $P_{11}(5/2)$ lines will also have contributions from higher odd partial waves ($l = 1,3,...$). The magnitude of the $\Delta N = 0$ peak relative to the $\Delta N = +2$ is hence expected to be larger for the $P_{11}(5/2)$ case than for the $P_{11}(3/2)$. This argument can be further elaborated by considering the rotational branching ratios expected in REMPI via the pure R_{21} ($J = 1/2,3/2,5/2,7/2$) lines. Branching ratios for these are shown in Fig. 2. In this case the F_2 component of the $J_i = J_A = 3/2$ level corresponds to $N_i = 2$, and the $l = 1$ and 3 partial waves therefore also contribute to $\Delta N = 0$. The relative branching ratios for $\Delta N = 0$ and 2 peaks hence would not be expected, as seen in Fig. 2, to show the strong decrease with J, in contrast to the behavior of the P_{11} lines.

The experimental ZEKE spectra of Fig. 1 show that the $\Delta N \neq 0$ peaks die off rapidly with increasing N_i. This behavior is in contrast to the calculated spectra. Although these spectra do show an initial decrease in the $\Delta N \neq 0$ peaks, the calculated relative peak heights approach the high-J limit by $N_i = 3$. This high-J limit ($J \cong 21.5$) of the branching ratios agrees with recent PES measurements.[2,4,5] This result implies that the observed low-J low-kinetic energy ratios, as seen in Figs. 1(a)–1(d) would ultimately have to increase with J so as to reproduce this high-J behavior.

Finally, the calculated $\Delta N =$ odd branching ratios are generally smaller than those seen experimentally. The selection rule in Eq. (5) shows that even photoelectron partial waves contribute to these peaks. The discrepancy between the calculated and measured branching ratios for the $\Delta N =$ odd peaks may be due to the threshold behavior of the $l = 0$ wave.

In Fig. 3, we show the rotationally resolved photoelectron angular distributions (PAD) for the spectra of Fig. 1. These have been normalized, so that $\beta_0 \equiv 1.00$. In the weak-field approximation the maximum β_L is β_4. The PADs are dramatically state-dependent. As predicted, the PAD for $N_i = N_+ = 0$, has a pure p-wave character. Note that the PADs for the same $|\Delta N|$'s, as a function of J, are similar for different J_i, reflecting similarities in the contributing waves of the continuum in the high-J limit.

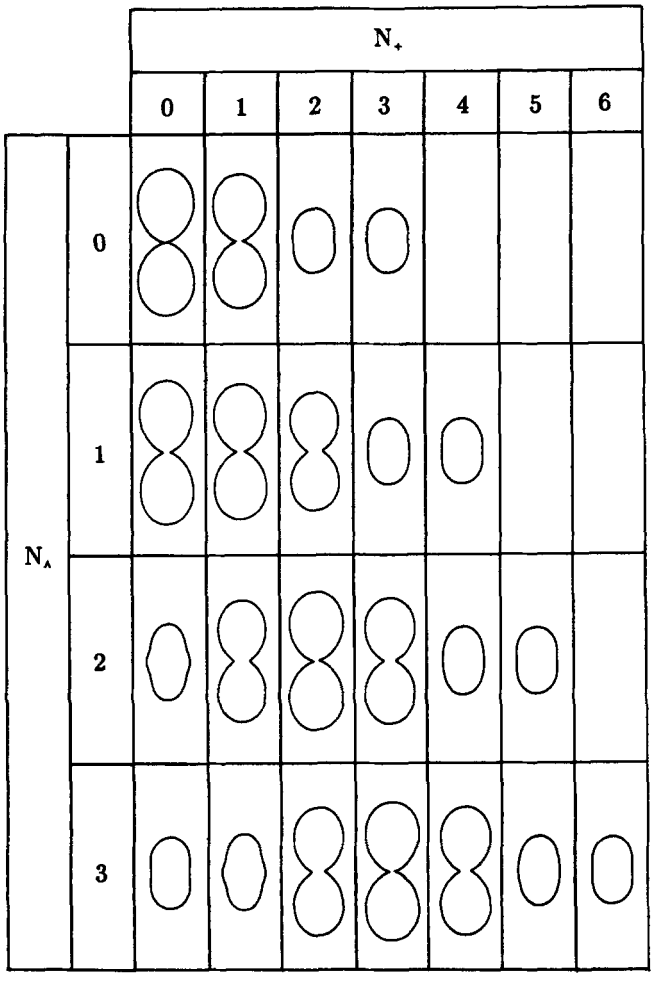

FIG. 3. Photoelectron angular distributions for REMPI via the $P_{11}(J)$ branches, $J = 3/2 - 9/2$, of the 0–0 band of the $X\,^2\Pi$–$A\,^2\Sigma^+$ transition as a function of N_A, where N_A is the rotational quantum number, less spin, of the intermediate state. $\theta = 0°$ is vertical.

IV. CONCLUSION

We have reported rotational branching ratios for very low photoelectron energies (50 meV) resulting from $(1+1')$ REMPI via low J levels of the $A\,^2\Sigma^+(3s\sigma)$ state of NO. Comparison with experimental spectra at zero-kinetic energy (ZEKE) of Sander *et al.*[7] shows good agreement for ionization through the $N_i = 0$ and 1 levels, but significant discrepancies remain for $N_i = 2$ and 3 where the rapid die off of the $\Delta N \neq 0$ peaks seen experimentally is not reproduced by the present results. A possible cause of this discrepancy is other state-dependent competing processes, such as autoionization and predissociation. The experimental spectra, however, do not seem to support the presence of autoionization.[7] The trends in the calculated branching ratios can also be understood in terms of simple angular momentum (l,N_i, N_+) changes in the ionization step. Calculated photoelectron angular distributions also show a strong dependence on ΔN reflecting the changing composition of the photoelectron wave function. These results serve to underscore the molecular nature of the photoionization process.

ACKNOWLEDGMENTS

This material is based on research supported by the National Science Foundation under Grant No. CHE-8521391, by AFOSR under Grant No. 87-0039, and by the Office of Health and Environmental Research of DOE (DE-FG03-87ER60513). The authors also acknowledge use of the resources of the San Diego SuperComputer Center which is supported by the National Science Foundation. Work done by S.N.D. was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48. H.R. gratefully acknowledges the support of the Danish Natural Science Research Council.

[1]S. T. Pratt, P. M. Dehmer, and J. L. Dehmer, J. Chem. Phys. **78**, 4315 (1983).
[2]W. G. Wilson, K. S. Wiswanathan, E. Sekreta, and J. P. Reilly, J. Phys. Chem. **88**, 672 (1984).
[3]J. E. Polland, D. J. Trevor, J. E. Recett, Y. T. Lee, and D. A. Shirley, J. Chem. Phys. **77**, 34 (1982).
[4]K. S. Wiswanathan, E. Sekreta, E. R. Davidson, and J. P. Reilly, J. Phys. Chem. **90**, 5078 (1986).
[5]S. Allendorf, D. Leahy, and R. N. Zare (private communication).
[6]K. Müller-Dethlefs, M. Sander, and E. W. Schlag, Chem. Phys. Lett. **112**, 291 (1984); Z. Naturforsch. Teil A **39**, 1089 (1984).
[7]M. Sander, L. A. Chewter, K. Müller-Dethlefs, and E. W. Schlag, Phys. Rev. A **36**, 4543 (1987).
[8]S. N. Dixit and V. McKoy, Chem. Phys. Lett. **128**, 49 (1986).
[9]S. N. Dixit, D. L. Lynch, V. McKoy, and W. M. Huo, Phys. Rev. A **32**, 1267 (1985).
[10]H. Rudolph, S. N. Dixit, V. McKoy, and W. M. Huo, Chem. Phys. Lett. **137**, 521 (1987).
[11]S. N. Dixit and V. McKoy, J. Chem. Phys. **82**, 3546 (1985).
[12]H. Rudolph, S. N. Dixit, V. McKoy, and W. M. Huo, J. Chem. Phys. **88**, 637 (1988).
[13]H. Rudolph, S. N. Dixit, V. McKoy, and W. M. Huo, J. Chem. Phys. **88**, 1516 (1988).
[14]L. T. Earls, Phys. Rev. **48**, 423 (1935).
[15]A. R. Edmonds, *Angular Momentum in Quantum Mechanics*, 2nd ed. (Princeton University, Princeton, NJ, 1974).
[16]K. Kaufmann, C. Nager, and M. Jungen, Chem. Phys. **95**, 385 (1985).
[17]R. R. Lucchese and V. McKoy, Phys. Rev. A **21**, 112 (1980).
[18]R. R. Lucchese, G. Raseev, and V. McKoy, Phys. Rev. A **25**, 2572 (1982).
[19]K. P. Huber and G. Herzberg, *Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979).