

$$q_n^+ \equiv q^+(S, M_s, A) = \sum_k \sum_l a_k^+ a_l X_{kl}(S, M_s, A), \quad (3)$$

labeled by the total spin quantum numbers S , M_s , and the absolute value A of the projection of the orbital angular momentum on the molecular axis. In this manner we obtain the electronic states $|0\rangle$, and $|n\rangle = q_n^+ |0\rangle$ as orthogonal and noninteracting across the electronic Hamiltonian. These properties are guaranteed for all states, even states of the same symmetry species, because of the consistency condition³ $q_n |0\rangle = 0$, being satisfied for the operators q_n .

The polarization propagator gives us direct information on vertical transition energies and electronic transition moments for all possible electronic transitions. In Fig. 1 we display the calculated transition moments $M_{nn'}(R)$ of the $B^3\Pi_g \rightarrow A^3\Sigma_u^+$ and the $B^3\Pi_g \rightarrow W^3\Delta_u$ as a function of the internuclear separation R . The vertical excitation energies at various R from the $X^1\Sigma_g^+$ AGP ground state generate excited state potential energy curves which are used to calculate numerical vibrational states. The radiative lifetime τ_{nvJ} of a particular vibrational v , rotational J state of the excited electronic state n can then be expressed in nanoseconds from the equation

$$\tau_{nvJ}^{-1} = 2.02607 \times 10^{-15} \times \sum_{n'v'J'} E^3(nvJ, n'v'J') \times |\langle vJ | M_{nn'}(R) | v'J' \rangle|^2 S_{J'}^J / (2J + 1), \quad (4)$$

where $S_{J'}^J$ are the Hönl-London factors⁶ and E is the excitation energy. The results given in Table I are not produced

with the appropriate averaging over rotational levels, but are calculated for the $J = 0, J' = 0$ transitions. We do not expect any significant change of results if proper averaging were carried out. Convergence of the sum over vibrational levels is checked by the "completeness" condition $\sum_{v'} |\langle v|v'\rangle|^2 \geq 0.92$, and limits our calculation to the first 14 vibrational levels. The calculated lifetimes of the B state going to the $W^3\Delta_u$ are approximately ten times longer and thus of no consequence.

Our reported lifetimes are calculated using the experimental excitation energies. When our calculated energy differences between the $B^3\Pi_g$ and the $A^3\Sigma_u^+$ were used the lifetimes were about a factor of 1/8 smaller. This situation is not unusual for theoretical calculations and is consistent with earlier applications of our model, i.e., the transition moments and the shapes of the potential energy curves are of higher quality than the excitation energies for a given primitive orbital basis. We are confident that a larger basis with more diffuse functions will yield better excitation energies and thus also better pure theoretical lifetimes.

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COMMENTS

Comment on "Three photon resonance ionization of H₂" [*J. Chem. Phys.* **77**, 877 (1982)]^{a)}

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In a recent paper¹ (hereafter referred to as I), Ritchie *et al.* presented calculations for two-photon resonant three-photon ionization of H₂ via the $E, F^1\Sigma_g^+$ state. The analysis was based on the extended two-level rate theory (ETLRT) of Eberly and O'Neil² in which the total ionization rate (in the notation of I) is given by

$$R_{3,0v',0J'} = \frac{\frac{1}{4}\Omega_{2,0v',0J'}^2 R_{1,J'0}}{\Delta_{2,0v',0J'}^2 + \frac{1}{2}\Omega_{2,0v',0J'}^2 + \frac{1}{4}R_{1,J'0}^2}, \quad (1)$$

where $\Omega_{2,0v',0J'}$ is the effective two-photon Rabi frequency

for the $00 \rightarrow v'J'$ transition, $\Delta_{2,0v',0J'}$ the detuning of two photons from resonance, and $R_{1,J'0}$ the total, angle-integrated, ionization rate out of $J', M' (= 0)$ resonant intermediate state. To discuss photoelectron angular distributions in the three-photon ionization process under consideration, Ritchie *et al.*¹ generalized Eq. (1) by replacing $R_{1,J'0}$ in both the numerator and denominator of Eq. (1) by the corresponding angle-resolved rate $R_{1,J'0}(\theta)$, where θ is the angle of ejection of the electron with respect to the polarization vector of the radiation (linear polarization was assumed in I). Thus the three-photon angular distribution as derived in I is

$$R_{3,0\nu',0J'}(\theta) = \frac{\frac{1}{4}\Omega^2_{2,0\nu',0J'} R_{1,J'0}(\theta)}{\Delta^2_{2,0\nu',0J'} + \frac{1}{2}\Omega^2_{2,0\nu',0J'} + \frac{1}{4}R_{1,J'0}^2(\theta)}. \quad (2)$$

In this Comment we will show that the above generalization is incorrect on both mathematical as well as physical grounds and leads to the erroneous results for $R_{3,0\nu',0J'}(\theta)$ shown in Figs. 3 and 5 of I.

We first point out some of the obvious inconsistencies in Eq. (2): (i) Integration of Eq. (2) over θ does not yield Eq. (1). (ii) In the parameter space defined by $R_1 \gg \Omega, \Delta$, Eq. (2) yields $R_{3,0\nu',0J'}(\theta) \sim [1/R_{1,J'0}(\theta)]$, which is unphysical. (iii) Based on Eq. (2) the authors claim that "for unsaturated transitions, the three-photon angular distribution is not given by the simple series in $\cos^n \theta$...". This is incorrect because, unsaturated weak field transitions from an isotropic ground state do yield photoelectron angular distributions that are simple power series in $\cos \theta$ and terminate at some maximum power n_{\max} . Furthermore, the existence of n_{\max} and the relationship $n_{\max} = 2N$ for N -photon ionization of a statistically distributed initial state follow purely from symmetry considerations and are independent of saturation effects. The influence of dynamics of the process appears as a variation (nonperturbative) of the coefficients of these power series.³ (iv) The process under consideration in I proceeds through a single bound channel, i.e., $\nu J = 0,0 \rightarrow \nu' J' = 3,0 \rightarrow \text{continuum}$ or $\nu J = 0,0 \rightarrow \nu' J' = 3,2 \rightarrow \text{continuum}$. As we shall show below, the normalized three-photon angular distribution in this case is identical to the single photon angular distribution out of the specific $J'M'(=0)$ intermediate state with saturation effects contributing an overall multiplicative factor in the absolute photoelectron angular distributions.

These inconsistencies arise due to the improper generalization of Eq. (1) assumed in writing Eq. (2). While modification of $R_{1,J'0}$ in the numerator of Eq. (1) to $R_{1,J'0}(\theta)$ is justified, the same generalization in the denominator is incorrect since $R_{1,J'0}$ appears in the denominator as a result of bound state dynamics which is only sensitive to the total loss of population to the continuum and not to the angle-resolved loss. We demonstrate this below using ETLRT and obtain the proper generalization of Eq. (1) to describe angular distributions.

In ETLRT² a system in an initial state $|0\rangle$ ionizes via a single near-resonant state $|1\rangle$. Denoting by Ω the Rabi (or the effective Rabi) frequency for the $|0\rangle \rightarrow |1\rangle$ transition, by Δ the detuning of the appropriate number of photons from the $|0\rangle \rightarrow |1\rangle$ resonance and by R_1 the ionization rate out of $|0\rangle$, the density matrix elements σ_{00} , σ_{11} , σ_{10} , and σ_{01} obey

$$\dot{\sigma}_{01} = - \left[\frac{R_1}{2} + i\Delta \right] \sigma_{01} - \frac{1}{2} i\Omega (2\sigma_{11} - n), \quad (3a)$$

$$\dot{\sigma}_{10} = - \left[\frac{R_1}{2} - i\Delta \right] \sigma_{10} + \frac{1}{2} i\Omega (2\sigma_{11} - n), \quad (3b)$$

$$\dot{\sigma}_{11} = - R_1 \sigma_{11} - \frac{1}{2} i\Omega (\sigma_{01} - \sigma_{10}), \quad (3c)$$

and

$$\dot{n} = - R_1 \sigma_{11}, \quad (3d)$$

respectively. In these equations, $n(t) = \sigma_{00} + \sigma_{11}$ and we have neglected laser bandwidths and spontaneous emission

rates in Eq. (3). Note further that the parameters Ω , Δ , and R_1 are the same as those used in Eq. (1) with the vibrational rotational indices suppressed. As shown in Ref. 2, ETLRT solves Eqs. (3a)–(3c) using the approximations

$$\dot{\sigma}_{01} = 0, \quad \dot{\sigma}_{10} = 0, \quad \text{and} \quad \dot{\sigma}_{11} = 0. \quad (4)$$

This yields for the population of the intermediate state

$$\sigma_{11} = \frac{\frac{1}{4}\Omega^2}{\Delta^2 + \frac{\Omega^2}{2} + \frac{1}{4}R_1^2} n. \quad (5)$$

Substitution of this result in Eq. (3d) gives

$$\frac{dn}{dt} = - \left[\frac{\frac{1}{4}\Omega^2 R_1}{\Delta^2 + \frac{\Omega^2}{2} + \frac{1}{4}R_1^2} \right] n. \quad (6)$$

This equation defines the ETLRT rate for the overall multiphoton ionization process.

Now, to determine the photoelectron angular distributions one has to write an equation of motion for the probability of ejection of a photoelectron $P(\theta)$ at an angle θ , with respect to the polarization vector of the light (assuming linear polarization). With $R_1(\theta)$ denoting the angle-resolved ionization rate out of $|1\rangle$, $P(\theta)$ obeys³

$$\dot{P}(\theta) = R_1(\theta)\sigma_{11}. \quad (7)$$

The total ionization probability is given by

$$P = 2\pi \int_0^\pi P(\theta) \sin \theta d\theta = 1 - n. \quad (8)$$

Substituting σ_{11} within ETLRT, as given by Eq. (5), into Eq. (7) one obtains

$$\dot{P}(\theta) = \frac{R_1(\theta)\frac{1}{4}\Omega^2}{\Delta^2 + \frac{\Omega^2}{2} + \frac{R_1^2}{4}} n. \quad (9)$$

Since $P(\theta)$ is not related in a simple way to n , Eq. (9) cannot be converted to a form similar to that in Eq. (6) which would enable one to extract an angle resolved rate like the angle integrated rate calculated with ETLRT. Physically, this difficulty reflects the fact that evolution of the bound state dynamics is only sensitive to the total loss of population to the continuum. However, in a less-than-rigorous way, one could, from Eq. (9), define an angle resolved "rate" for the process as

$$R(\theta) = \frac{R_1(\theta)\frac{1}{4}\Omega^2}{\Delta^2 + \frac{1}{2}\Omega^2 + \frac{R_1^2}{4}} \quad (10)$$

to obtain a generalization of the ETLRT rate to include angular distributions. Note that Eq. (10) does not have the inconsistencies implied by Eq. (2). More importantly, Eqs. (9) and (10) demonstrate the fact that for photoelectron angular distributions in multiphoton ionization proceeding via a single bound state channel ($|0\rangle \rightarrow |1\rangle \rightarrow \text{ionization}$), the saturation effects simply introduce an overall multiplicative factor and do not change the shape of the distribution. Thus, in Figs. 3 and 5 of I the $R_{3,0\nu',0J'}(\theta)$ curves should be parallel to, but shifted from, the corresponding $R_{1,J'0}(\theta)$ curves. In Fig. 3 of I they appear almost parallel since, for this case $\Omega \gg R_1(\theta)$

and the θ dependence in the denominator (though incorrect) is insignificant. The discrepancy between the $R_{1,J^0}(\theta)$ and $R_{3,0^0,0^0}(\theta)$ curves in Fig. 5, on the other hand, is completely artificial and arises due to the presence of the θ dependence in the denominator of Eq. (1) of I. For multiphoton ionization proceeding via many bound state channels as would be the case with several near-resonant intermediate states and/or different M states in the initial state, the relative saturation rates in various channels would be different and this would give rise to changes in the shape of the angular distribution as we have demonstrated recently in atomic multiphoton ionization.^{3,4} Such studies in molecular multiphoton ionization are in progress.

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³Equation (7) follows quite rigorously from the equations of motion for the density matrix ($d\rho/dt = i[H,\rho]$) after an adiabatic elimination of density matrix elements between $|1\rangle$ and the continuum in the right-hand side. For details of this procedure see the Appendix in S. N. Dixit and P. Lambropoulos, *Phys. Rev. A* **27**, 861 (1983).

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ERRATA

Erratum: Proton chemical shift tensors in hydrogen-bonded dimers of RCOOH and ROH [*J. Chem. Phys.* **79**, 4958 (1983)]

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Due to publication errors, several paragraphs in this manuscript were printed incorrectly. The correct paragraphs are:

p. 4960, 4961...

Experimentally, it is found that the principal axis system of a hydrogen-bonded proton shielding tensor corresponds approximately to the geometry of that hydrogen bond, i.e., the most shielded direction is nearly parallel to the axis of the hydrogen bond. The chemical shift tensor is only roughly axially symmetric, since the two perpendicular components are not usually equal. The direction perpendicular to the "plane" of the hydrogen bond system, when it can be so defined, is the least shielded. A simple diamagnetic argument,²⁵ illustrated in Fig. 3, explains these results. For a hydrogen-bonded dimer in an external magnetic field, local atomic currents of the proton acceptor oxygen induce fields that reinforce the fields already present in the monomer due to similar currents on the proton donor oxygen. The strength of these induced fields is proportional to the electron density on the oxygen atoms. An increase in shielding for the proton in the parallel direction and a decrease in the perpendicular directions result.

p. 4961, 4962...

Berglund and Vaughan considered several correlations between the deuterium quadrupole coupling constant e^2qQ/h and components of the proton shielding tensor. However, the e^2qQ/h results are obtained from deuterated crystals and, obviously, the proton chemical shifts are for crystals with their hydrogens intact. The O-D bond length will differ from the O-H bond length, as will the O...O separation, so

there seems little justification in looking for a quantitative relationship between empirically determined e^2qQ/h 's and empirically determined proton shielding tensors. In fact, replacing e^2qQ/h with a parameter of the undeuterated crystal $R_{O...O}$ in Berglund and Vaughan's plots yields better linear correlations in all cases! The reason there is any correlation at all between e^2qQ/h and $\bar{\sigma}$ or σ_1 is due to the strong linear dependences of all three quantities with $R_{O...O}$. Although most theoretical and experimental studies have concentrated on the relationship between e^2qQ/h and the D...O distance in O-D...O "hydrogen" bonds, some investigations have indicated a strong linear component to the dependence of e^2qQ/h on $R_{O...O}$.²⁷⁻³⁰ It would be worthwhile to further pursue this matter for the hydrogen-bonded dimers of RCOOH and ROH presented here, but for reasons enumerated in the next section, this was not done. Hence only correlations between $R_{O...O}$ and components of the proton shielding tensor are considered here.

p. 4964...

Examining these tensors for the monomer proton donors of dimers I and IV, it is seen that, for ROH or for RCOOH, σ_{xx} and σ_{yy} are roughly constant but that σ_{zz} varies. Hence it appears that σ_{zz} is the most affected by the nature of the R substituent. Since σ_{zz} is so sensitive to these oxygen ligands in the proton donor monomer, it is not surprising to find a lack of correlation between σ_{\parallel} and $R_{O...O}$ in the dimers. Since σ_{xx} and σ_{yy} are relatively insensitive to the nature of the substituent in the proton donor monomer, it is reasonable that σ_1 might correlate with $R_{O...O}$ since the latter is a measure of the strength of the hydrogen bonding interaction.