Two-photon dissociation of vibrationally excited HD\(^+\): The inhomogeneous differential equation approach

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(Received 3 February 1986; accepted 23 April 1986)

We extend the inhomogenous-differential-equation (IDE) approach of Dalgarno and Lewis for a detailed study of two-photon dissociation (TPD) of HD\(^+\) from high vibrational levels of the 1\(\sigma_g\) electronic state. Contrary to the H\(_2^+\) case, where the TPD cross sections \(\sigma^{(2)}_{ij}\) are largest near TPD thresholds and decrease monotonically with increasing photon energy, the HD\(^+\) cross sections are characterized by rich resonant and interference structures. We present \(\sigma^{(2)}_{ij}\) results for TPD from the initial \(v_i = 6, 8, 10, 12, 14, 16, \) and \(j_i = 0\) levels as well as from \(v_i = 14, j_i = 0, 2, 4\) levels for a wide range of wavelengths of linearly polarized radiation accessible by CO\(_2\) and CO lasers. It is found that while there are four TPD pathways, the channel 1\(\sigma_g\) \(\to 1\sigma_g\) dominates the two-photon process in most of the cases we have studied. Further, the results show that \(\sigma^{(2)}_{ij}\) increases rather rapidly as the initial vibrational quantum number \(v_i\) increases, indicating that the heteronuclear diatomic molecules in high vibrational levels can be efficiently two-photon dissociated by IR lasers. Consequently molecular structures near the dissociation limit may be conveniently probed by two-photon spectroscopy—as has indeed been demonstrated recently by experiments. Our \(\sigma^{(2)}_{ij}\) results thus provide complementary information to the HD\(^+\) spectroscopic data obtained recently by Carrington et al.

I. INTRODUCTION

Multiphoton dissociation (MPD) of molecules by electromagnetic radiation is a subject of much current interest.\(^\text{1}\) The ease of MPD depends upon the vibrational density of states and the size of the molecule. While more than 100 molecules—from 3 to 62 atoms in size—have been observed undergoing multiphoton absorptions, MPD of a ground vibrational state of a diatomic molecule has never been observed due to the anharmonicity bottleneck. The estimated required intensities for observable dissociation of diatomic molecules exceed \(10^{13}\) W/cm\(^2\). At these high field strengths ionization and electric breakdown of the gas would probably occur first.\(^\text{2}\)

In contrast, MPD from high vibrational levels of diatomic molecules can be achieved efficiently as recently demonstrated experimentally.\(^\text{3}\) Using CO and CO\(_2\) lasers, Carrington et al.\(^\text{3}\) have observed two-photon dissociation of HD\(^+\) from \(v_i = 14\) and 16, respectively. These high-resolution spectroscopic studies provide accurate structure information near the dissociation limit.

From a theoretical point of view, while a perturbative technique\(^\text{4}\) is available for the treatment of MPD processes, there remains the difficulty of carrying out the explicit summation over the complete vibrational intermediate states in a converged way even for the simplest molecule\(^\text{5}\) like H\(_2^+\). To circumvent this difficulty, we have recently extended the inhomogenous differential equation (IDE) method of Dalgarno and Lewis\(^\text{6}\) for implicit numerical evaluation of the infinite sum over vibrational intermediate states. The method was applied\(^\text{7}\) to two-photon dissociation (TPD) of vibrationally excited H\(_2^+\) (1\(\sigma_g\)). The H\(_2^+\) TPD cross sections are very small for low-lying vibrational states but increase rapidly with increasing vibrational quantum number. The IDE method was found to be capable of providing converged weak-field TPD rates rapidly. This method has also been previously used in the study of (bound–bound) Raman scattering in diatomic molecules.\(^\text{8}\)

Motivated by the recent experimental observations,\(^\text{3}\) we extend in this paper the IDE method to the study of two-photon dissociation of HD\(^+\) from high vibrational levels. Some preliminary results of the HD\(^+\) two-photon dissociation cross section \(\sigma^{(2)}\) have been reported previously.\(^\text{9}\) Contrary to the H\(_2^+\) case, where \(\sigma^{(2)}\) are largest near two-photon dissociation threshold and decrease monotonically with increasing photon energy, the HD\(^+\) cross sections are dominated by rich resonant structures. Another perturbation calculation of two-photon dissociation of HD\(^+\) has recently appeared\(^\text{10}\) using the explicit summation method of Ref. 4. They used A \(\cdot\) P coupling for the interaction Hamiltonian but reported results for \(v_i = 6\) and in nonresonant frequency regions only. We note in passing that while our interest here is to carry out weak-field (intensity-independent) TPD cross sections using the IDE method, the development of nonperturbative techniques for strong-field MPD\(^\text{7,11,12}\) and Raman scattering\(^\text{13}\) processes is a subject of current theoretical efforts.

In the following section (Sec. II) we shall discuss the IDE method appropriate for two-photon dissociation calculations of heteronuclear diatomic molecules. The method is applied to HD\(^+\) and the results are presented in Sec. III.
II. METHOD

The theory of two-photon dissociation of heteronuclear diatomic molecules will be briefly described below. We assume that the light intensity is such that the molecule-photon interaction may be treated as a perturbation. Then, to second order in perturbation theory, the probability per unit time that a molecule in an initial bound state \(i\) will absorb two photons of frequency \(\omega\) and make a transition to a final continuum state \(f\), dissociating in the solid angle \(d\Omega\), with momentum \(k\), is given by

\[
dW_{ij}^{(2)} = (M \sigma^2 / \hbar) \alpha^3 \omega^2 |T_{ji}|^2 d\Omega_k,
\]

where \(M\) is the reduced mass of the dissociating particles, \(\alpha\) the fine structure constant, \(I\) the incident photon flux, and \(T_{ji}\) is the transition matrix element. The total transition rate \(W_{ji}^{(2)}\) is obtained by averaging over the initial rotational magnetic quantum numbers \(m_i\) and integrating over all solid angles:

\[
W_{ji}^{(2)} = \frac{M \sigma^2 \omega^3 k^2 I}{\hbar} \sum_{2j_i} \left| T_{ji} \right|^2 d\Omega_k.
\]

For clarity of notation, we shall now confine our discussion to the specific case of two-photon dissociation of HD\(^+\) (Fig. 1). Only the initial \(1\sigma_g\) ground electronic state and the \(2\sigma_u\) excited electronic state are considered. This should be a good approximation here as other excited electronic states lie much higher in energy.

We assume the Born–Oppenheimer approximation, so that the total (field-free) molecular wave function \(\chi_n (r, R)\), solution of either the \(1\sigma_g\) or \(2\sigma_u\) electronic state, can be written as

\[
\chi_n (r, R) = \Phi_n (r, R) \psi_n (r, R).
\]

Here \(r\) and \(R\) are, respectively, the electronic and nuclear coordinates, and the electronic wave function \(\psi_n (r, R)\) depends parametrically on \(R\). For a diatomic molecule, we can further write the nuclear wave function \(\Phi_n (R)\) as a product of vibrational, \(\phi_\nu (R)\), and rotational \(Y_{jm} (\hat{R})\), wave functions,

\[
\Phi_n (R) = \phi_\nu (R) Y_{jm} (\hat{R}).
\]

Then \(R\phi_\nu (R)\) satisfies the eigenvalue equation

\[
\left[ \frac{d^2}{dR^2} - \frac{j(j + 1)}{R^2} + \frac{2M}{\hbar^2} \left( E_{\nu} - U_n (R) \right) \right] R\phi_\nu (R) = 0,
\]

where \(U_n (R)\) is the electronic energy at internuclear separation \(R\) of either the \(1\sigma_g\) \((n = 1)\) or the \(2\sigma_u\) \((n = 2)\) electronic state as depicted in Fig. 1.

The transition matrix element \(T_{ji}\) in Eq. (1) is given by

\[
T_{ji} = \sum_n \left( \begin{array}{c} f \mid D \cdot \epsilon | i \end{array} \right) \langle n \mid D \cdot \epsilon | i \rangle \frac{E_{\nu} - E_i - \hbar \omega}{E_{\nu} - E_i - \hbar \omega},
\]

where \(\epsilon\) is the unit polarization vector of the absorbed photons, \(D\) is the dipole moment operator, and the sum over \(n\) includes all bound and continuum rovibrational states \(|ujm\rangle\) of the \(1\sigma_g\) electronic state and all continuum rovibrational states \(|ujm\rangle\) of the \(2\sigma_u\) electronic state. The initial state \(|i\rangle\) is assumed to be in a rovibrational bound state \(|ujm_i, \omega_i\rangle\) of the \(1\sigma_g\) electronic state and the final state \(|f\rangle\) can be a rovibrational continuum state of either the \(1\sigma_g\) or the \(2\sigma_u\) electronic state. The final continuum state \(|f\rangle\) has the partial wave expansion

\[
|f\rangle = 4\pi \sum_{j', m_j} \frac{Y_{jm} (R)}{\sqrt{2j' + 1}} |j', m_j, \omega_f\rangle \cdot \phi_{k', j'} (R) Y_{jm}^* (R) Y_{jm}^* (\hat{k})
\]

where \(k\) is the total momentum of the two-photon absorption event.

For the two-photon dissociation to the \(1\sigma_g\) continuum, the transition matrix element, Eq. (6), can be written as

\[
T_{ji}^{(1)} (1\sigma_g) = t_1^{(1)} + t_2^{(1)},
\]

and to the \(2\sigma_u\) continuum,

\[
T_{ji}^{(2)} (2\sigma_u) = t_1^{(1)} + t_2^{(1)}.
\]

Here

\[
\begin{align*}
t_1^{(1)} &= \sum_{j, m_j} \sum_{ujm} \left( \begin{array}{c} kj, m_j (1\sigma_g) \mid \mu_{\nu} C_q^{(1)} |ujm (1\sigma_g) \rangle \langle ujm (1\sigma_g) \mid \mu_{\nu} C_q^{(1)} |vj, m_i (1\sigma_g) \rangle \right) \frac{E_{uj} - E_{\nu, \omega} - \hbar \omega}{E_{uj} - E_{\nu, \omega} - \hbar \omega}, \\
t_2^{(1)} &= \sum_{j, m_j} \sum_{ujm} \left( \begin{array}{c} kj, m_j (1\sigma_g) \mid \mu_{\nu} C_q^{(1)} |ujm (2\sigma_u) \rangle \langle ujm (2\sigma_u) \mid \mu_{\nu} C_q^{(1)} |vj, m_i (1\sigma_g) \rangle \right) \frac{E_{uj} - E_{\nu, \omega} - \hbar \omega}{E_{uj} - E_{\nu, \omega} - \hbar \omega},
\end{align*}
\]
\begin{align}
t_3^{(q)} &= \sum_{j, m_f, m_i, \nu, \sigma} \frac{\langle k j m_f (2p\sigma) | \hat{\mu}_D C_q^{(1)}(1st) | v m_i (1\sigma) \rangle \langle v m_f (2p\sigma) | \hat{\mu}_T C_q^{(1)}(1st) | u j m_i (1\sigma) \rangle}{E_{qj} - E_{n_i} - \hbar \omega}, \\
t_4^{(q)} &= \sum_{j, m_f, m_i, \nu, \sigma} \frac{\langle k j m_f (2p\sigma) | \hat{\mu}_T C_q^{(1)}(1st) | v m_i (1\sigma) \rangle \langle v m_f (1\sigma) | \hat{\mu}_D C_q^{(1)}(1st) | u j m_i (1\sigma) \rangle}{E_{qj} - E_{n_i} - \hbar \omega},
\end{align}

where the electric dipole operator \( D \) has been written
\[ D = \hat{D} C_q^{(1)}. \]

\( C_q^{(1)} \) is the spherical tensor operator of unit rank and \( q \) is the photon polarization index. In Eq. (9), \( \hat{\mu}_D (R) \) and \( \hat{\mu}_T (R) \) are, respectively, the permanent and the transition dipole operators given by
\[ \hat{\mu}_D (R) = \langle \psi_a (r; R) | \hat{D} | \psi_a (r; R) \rangle, \quad n = 1s\eta \text{ or } 2p\sigma, \]
and
\[ \hat{\mu}_T (R) = \langle \psi_{1s\eta} (r; R) | \hat{D} | \psi_{2p\sigma} (r; R) \rangle. \]

Owing to the dipole selection rule, only terms with \( j = j_i \pm 1 \) and \( j_f = j \pm 1 \) will contribute to the \( T_n^{(q)} \). Carrying out the angular integrations in Eq. (9), we find
\begin{align}
t_a^{(q)} &= 4\pi \sum_{\nu, j_f, j_i} (-1)^{j_i} \exp(-i\delta_{j_f, j_i}) \sum_{m_f, m_i} Z^{(j_f, j_i)}(m_f, q, m_i) S_a(k j_f, j_i, j_f, j_i, Y_{j_f, j_i}(\hat{R})), \\
\end{align}
where
\begin{align}
Z^{(j_f, j_i)}(m_f, q, m_i) &= \langle Y_{j_f, j_i}(\hat{R})|C_q^{(1)}|Y_{m_i}(\hat{R})\rangle \langle Y_{m_i}(\hat{R})|C_q^{(1)}|Y_{j_f}(\hat{R})\rangle,
\end{align}
and the \( S_a \) are defined by
\begin{align}
S_1(k j_f, j_i, j_f, j_i, j_f) &= \sum_{\nu} \frac{\langle \phi_{kj_f, 1s\sigma} | \hat{\mu}_D | \phi_{qj_i, 1s\sigma} \rangle \langle \phi_{qj_i, 1s\sigma} | \hat{\mu}_D | \phi_{nu_i, 1s\sigma} \rangle}{E_{qj} - E_{n_i} - \hbar \omega}, \\
S_2(k j_f, j_i, j_f, j_i, j_f) &= \sum_{\nu} \frac{\langle \phi_{kj_f, 1s\sigma} | \hat{\mu}_T | \phi_{qj_i, 1s\sigma} \rangle \langle \phi_{qj_i, 1s\sigma} | \hat{\mu}_T | \phi_{nu_i, 1s\sigma} \rangle}{E_{qj} - E_{n_i} - \hbar \omega}, \\
S_3(k j_f, j_i, j_f, j_i, j_f) &= \sum_{\nu} \frac{\langle \phi_{kj_f, 2p\sigma} | \hat{\mu}_D | \phi_{qj_i, 2p\sigma} \rangle \langle \phi_{qj_i, 2p\sigma} | \hat{\mu}_D | \phi_{nu_i, 1s\sigma} \rangle}{E_{qj} - E_{n_i} - \hbar \omega}, \\
S_4(k j_f, j_i, j_f, j_i, j_f) &= \sum_{\nu} \frac{\langle \phi_{kj_f, 2p\sigma} | \hat{\mu}_T | \phi_{qj_i, 2p\sigma} \rangle \langle \phi_{qj_i, 2p\sigma} | \hat{\mu}_T | \phi_{nu_i, 1s\sigma} \rangle}{E_{qj} - E_{n_i} - \hbar \omega}.
\end{align}

Since
\[ \langle Y_{n_i}(\hat{R})|C_q^{(1)}|Y_{j_f}(\hat{R})\rangle = (-1)^{j_i-m} \begin{pmatrix} j & 1 & j_i \\ -m & q & m_i \end{pmatrix} \langle j||C_q^{(1)}||j_i\rangle, \]

it follows that in Eqs. (11) and (12) we must have
\[ m = q + m_i, \quad m_f = q + m = 2q + m_i. \]

For linearly polarized light, \( q = 0 \), we have further \( m_f = m = m_i \), and
\begin{align}
Z^{(j_f, j_i)}(m_f, 0, m_i) &= (2j_f + 1)\sqrt{(2j_i + 1)(2j_f + 1)} \begin{pmatrix} j_f & 0 & j_f \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} j & 1 & j \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} j_f & 0 & j_f \\ 0 & 0 & 0 \end{pmatrix} = \begin{pmatrix} j_f & 0 & j_f \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} j & 1 & j \\ 0 & 0 & 0 \end{pmatrix}.
\end{align}

Substituting Eqs. (8)–(13) into Eq. (2), and carrying out integration over all solid angles, one gets for the two-photon dissociation cross section to the \( 1s\sigma \) continuum,
\begin{align}
\sigma_q^{(1s\sigma)}(1s\sigma) &= \frac{16\pi^2 \alpha^2 \omega^2 k / \hbar}{2j_i + 1} \sum_{m_i} \mathcal{Q}_1(q, m_i),
\end{align}
where \( \nu, j_i \) signifies the initial bound state of the \( 1s\sigma \) electronic state, and
\begin{align}
\mathcal{Q}_1(q, m_i) &= Z_1 \left[ S_1(k j_f, 2j_i, j_i, j_f, j_i) \right] + \mathcal{Z}_2 \left[ S_2(k j_f, j_i, j_f, j_i, j_f) + S_2(k j_f, j_i, j_f, j_i, j_f) \right] \\
&\quad + \mathcal{Z}_3 \left[ S_1(k j_f, 2j_i, j_i, j_f, j_i) \right] + \mathcal{Z}_4 \left[ S_4(k j_f, j_i, j_f, j_i, j_f) \right].
\end{align}
Here for convenience we have defined
\[ Z_1(q,m) = Z^{(j_s+j_l+1, j_l)}(m, q, m), \]
\[ Z_2(q,m) = Z^{(j_s+j_l+1, j_l)}(m, q, m), \]
\[ Z_3(q,m) = Z^{(j_s+j_l-1, j_l)}(m, q, m), \]
and
\[ Z_4(q,m) = Z^{(j_s-2,j_l+1, j_l)}(m, q, m). \]
Similarly for two-photon dissociation to the 2p\(\sigma_u\) continuum, we obtain
\[ \sigma_q^{(n,j)}(2p\sigma_u) = \frac{16\pi^2\alpha^2\omega^2k/k}{2j + 1} \sum_m Q_{n,j}(q, m), \]
where \(Q_{n,j}\) can be obtained from \(Q_i\) in Eq. (17) by simply replacing \(S_1\) by \(S_3\) and \(S_2\) by \(S_4\). The angular factors \(Z_i\) in Eq. (18) can be conveniently written in terms of the initial rotational quantum numbers \((j_s, m_s)\). Thus in the case of linearly polarized light \((q = 0)\), for example, one finds
\[ Z_1 = \left( \frac{(j_s + m_s + 2)(j_s - m_s + 2)(j_s + m_s + 1)(j_s - m_s + 1)}{(2j_s + 5)(2j_s + 3)(2j_s + 1)} \right)^{1/2}, \]
\[ Z_2 = \frac{(j_s + m_s + 1)(j_s - m_s + 1)}{(2j_s + 3)(2j_s + 1)}, \]
\[ Z_3 = \frac{(j_s + m_s)(j_s - m_s)}{(2j_s + 1)(2j_s - 1)}, \]
and
\[ Z_4 = \left( \frac{(j_s + m_s - 1)(j_s - m_s - 1)(j_s + m_s)(j_s - m_s)}{(2j_s - 1)^2(2j_s - 3)(2j_s + 1)} \right)^{1/2}. \]

Equations (16) and (19) show that the calculation of two-photon cross sections can be reduced to the evaluation of \(S_n(kj_s,j_l,m; j_s)\) defined in Eq. (13). The summation over \(\nu\) in Eq. (13) is over all intermediate bound and continuum vibrational states and is in general difficult to perform accurately. To circumvent this difficulty, we shall use the inhomogeneous differential equation (IDE) method.\(^6\) Following Dalgarno and Lewis,\(^6\) we write
\[ S_n(kj_s,j_l,m; j_s) = \langle \phi_{\nu_l}(1s\sigma) | \hat{\mu}_D | \chi_{\nu_n}^{(T)}(R) \rangle, \]
and
\[ S_n(kj_s,j_l,m; j_s) = \langle \phi_{\nu_l}(2p\sigma) | \hat{\mu}_D | \chi_{\nu_n}^{(T)}(R) \rangle, \]
where
\[ \chi_{\nu_n}^{(T)}(R) = \sum_{\tilde{\nu}} \langle \phi_{\tilde{\nu}}(2p\sigma) | \hat{\mu}_T | \phi_{\nu_n}(1s\sigma) \rangle \cdot \phi_{\nu}(2p\sigma) \]
is the well-behaved solution of the inhomogeneous differential equation
\[ \frac{d^2}{dR^2} - \frac{j(j + 1)}{R} \]
\[ + \frac{2M}{\hbar^2} \left[ E_{\nu_n} + \hbar\omega - U_{2p\sigma}(R) \right] \right] \chi_{\nu_n}^{(T)}(R) \]
\[ = - \left( 2M/\hbar^2 \right) \mu_T(\hat{R}) R \phi_{\nu_n}(R). \]

Similarly \(S_1\) and \(S_4\) can be obtained by defining
\[ \chi_{\nu_n}^{(D)}(R) = \sum_{\tilde{\nu}} \langle \phi_{\tilde{\nu}}(1s\sigma) | \hat{\mu}_D | \phi_{\nu_n}(1s\sigma) \rangle \cdot \phi_{\nu}(1s\sigma), \]
so that
\[ S_1(kj_s,j_l,m; j_s) = \langle \phi_{\nu_l}(1s\sigma) | \hat{\mu}_D | \chi_{\nu_n}^{(D)}(R) \rangle \]
and
\[ S_4(kj_s,j_l,m; j_s) = \langle \phi_{\nu_l}(2p\sigma) | \hat{\mu}_D | \chi_{\nu_n}^{(D)}(R) \rangle, \]
where \(\chi_{\nu_n}^{(D)}(R)\) satisfies the IDE:
\[ \frac{d^2}{dR^2} - \frac{j(j + 1)}{R^2} \]
\[ + \frac{2M}{\hbar^2} \left[ E_{\nu_n} + \hbar\omega - U_{2p\sigma}(R) \right] \right] \chi_{\nu_n}^{(D)}(R) \]
\[ = - \left( 2M/\hbar^2 \right) \mu_D(\hat{R}) R \phi_{\nu_n}(R). \]

Equations (24) and (28) can be accurately integrated numerically for \(\chi_{\nu_n}^{(T)}(R)\) and \(\chi_{\nu_n}^{(D)}(R)\). The bound \(\phi_{\nu_n}(R)\) and continuum \(\phi_{\nu}(R)\) are also determined numerically by the Numerov method.\(^16\) Finally \(S_n(kj_s,j_l,m; j_s)\) can be computed from Eqs. (21), (22), (26), and (27) by numerical quadrature.

III. CALCULATIONS AND RESULTS

We have calculated two-photon dissociation cross sections for vibrationally excited levels of the ground 1s\(\sigma_g\) electronic state of HD\(^+\) for photon frequencies in the range \(\Delta\omega_0(D_0)\), where \(D_0\) is the dissociation energy (Fig. 1). The analysis of the Schrödinger equation for HD\(^+\) (H\(_2^+\)) is well documented.\(^17\) The adiabatic electronic energy curves for the 1s\(\sigma_g\) and 2p\(\sigma_u\) states and the transition dipole moment \(\mu_T(R)\) (1s\(\sigma_g\) to 2p\(\sigma_u\)) are calculated using a two-cen-
The accuracy of the potential energy curves and the transition dipole moment is comparable to those reported by Madsen and Peek\textsuperscript{19} and Ramaker and Peek,\textsuperscript{20} respectively. The permanent dipole moment $\mu(R)$, which is the same for the $1s\sigma_g$ and $2p\pi_u$ states in the conventional adiabatic approximation, is determined by the method described by Bunker.\textsuperscript{21,22} Nonadiabatic, relativistic, and hyperfine interactions are not considered here. They affect somewhat the high lying energy level positions near the dissociation limit. However, apart from causing slight shifts in transition frequencies, these interactions have little effect on the two-photon dissociation cross section calculations.
We have previously presented two-photon dissociation cross sections for the vibrational levels $v_1 = 6, 8, 10,$ and $12$ (all with $j_1 = 0$) of $\text{H}_2^+$ ($1\sigma_g^-$). Since $\text{H}_2^+$ has no permanent dipole moment, $\mu_\sigma(R) = 0$, it follows that $S_2$ in Eq. (13) is the only nonzero term in $\sigma^{(2)}$. As $2p_\sigma$, is a repulsive electronic state it therefore cannot be reached from the $1s\sigma_g$ ground electronic state by absorption of a photon with energy $h\omega < D_0$. Thus there are no resonances in the two-photon dissociation cross sections for $\text{H}_2^+$ and, in fact, it is found that $\sigma^{(2)}$ decreases monotonically as the photon energy is increased from its threshold value of $h\omega = 2D_0$ to $h\omega = D_0$.

The situation in $\text{HD}^+$ is quite different, because it has a permanent dipole moment, $\mu_\sigma(R) \neq 0$, which allows transitions to intermediate vibration–rotation levels of $1s\sigma_g$ elec-

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**FIG. 4.** $\sigma^{(2)}$ from the $(v = 10, j_1 = 0)$ level of $\text{HD}^+$ ($1s\sigma_g$).

**FIG. 5.** $\sigma^{(2)}$ from the $(v = 12, j_1 = 0)$ level of $\text{HD}^+$ ($1s\sigma_g$).
tronic state. When the photon frequency is such that \( \hbar \omega \approx E_{v}'(1\sigma_g) - E_{v,j}(1\sigma_g) \) for some values of quantum numbers \( v \) and \( j \), a resonance will occur in the cross section. This is illustrated in Figs. 2 to 7 where we have plotted the total cross section

\[
\sigma_i^{(v,j)} = \sigma_i^{(v,j)}(1\sigma_g) + \sigma_i^{(v,j)}(2\sigma_u)
\]

for \( v_i = 6, 8, 10, 12, 14, 16 \) and \( j_i = 0 \), where the subscript \( L \) stands for the linearly polarized light. As the initial rotational quantum number \( j_i \) is zero, there is only one resonance channel corresponding to \( j = 1 \) for each intermediate vibrational quantum number \( v \). For each \( v_i \), we have shown the first four allowable resonances and their interference.
TABLE 1. An example of the relative contribution of TPD matrix elements $S_k(\lambda)$, Eq. (13), (a = 1,2,3,4), to the cross section $\sigma_L^{(2)}$. $\sigma_L^{(2)}(1s\sigma_g)$ and $\sigma_L^{(2)}(2p\sigma_u)$ are the partial cross sections to the $1s\sigma_g$ and $2p\sigma_u$ continua, respectively. Shown here is the case for the TPD: ($v_i = 14$, $j_i = 0$) $\rightarrow$ ($v = 17$, $j = 1$) $\rightarrow$ ($\Delta v = 0$). The cross sections are in units of $10^{-50}$ cm$^4$ s$^{-1}$.

<table>
<thead>
<tr>
<th>$\lambda (\mu)$</th>
<th>$S_1$</th>
<th>$S_2$</th>
<th>$S_3$</th>
<th>$S_4$</th>
<th>$\sigma_L^{(2)}(1s\sigma_g)$</th>
<th>$\sigma_L^{(2)}(2p\sigma_u)$</th>
<th>$\sigma_L^{(2)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.51*</td>
<td>-0.382( +2)$^d$</td>
<td>0.110( -1)</td>
<td>0.437( +1)</td>
<td>-0.245( +4)</td>
<td>0.650</td>
<td>0.267( +4)</td>
<td>0.267( +4)</td>
</tr>
<tr>
<td>4.96*</td>
<td>-0.730( -2)</td>
<td>0.476( -2)</td>
<td>0.905( +1)</td>
<td>-0.286( +4)</td>
<td>0.433( -8)</td>
<td>0.257</td>
<td>0.257</td>
</tr>
<tr>
<td>4.66$^c$</td>
<td>0.311</td>
<td>0.299( -2)</td>
<td>0.124( +2)</td>
<td>-0.120( +2)</td>
<td>0.828( -4)</td>
<td>0.123( -3)</td>
<td>0.206( -3)</td>
</tr>
</tbody>
</table>

*Near-resonance region.
$^b$Off-resonance region.
$^c$Interference region.
$^d$ $-0.382( +2) = -0.382 \times 10^{-2}$.

structures. As IDE is a perturbative approach, $\sigma_L^{(2)}$ becomes infinite at each exact resonance position due to the vanishing of the energy denominator. Figures 2 to 7 show that $\sigma_L^{(2)}$ increases rather rapidly in both resonant and nonresonant frequency regions as the initial vibrational quantum number $v_i$ increases.

The relative contributions of $S_1$, $S_2$, $S_3$, and $S_4$ [defined in Eq. (13)] to the two-photon dissociation (TPD) total cross section $\sigma_L^{(2)}$ depends upon what frequency range we are looking at. Table 1 shows a typical example. In general, the nonresonance terms $S_2$ and $S_4$ contribute to the smoothly varying background and to the interference region only, and $|S_1|\leq |S_2|$. Of the two resonance terms $S_1$ (to the $1s\sigma_g$ continuum) and $S_4$ (to the $2p\sigma_u$ continuum), the latter dominates in all cases we have examined. This may be understood in terms of the greater magnitude of $\mu_T(R)$ as compared to $\mu_P(R)$ and in terms of the overlap of the high-lying near-resonance intermediate vibrational levels $\phi_{9j}(1s\sigma_g)$ with the dissociating $\phi_{9j}(2p\sigma_u)$ and $\phi_{9j}(1s\sigma_g)$ continuum levels. Due to the nature of the $U_{1s\sigma_g}(R)$ and $U_{2p\sigma_u}(R)$ potential curves, $\phi_{9j}(1s\sigma_g)$ oscillates more rapidly in the overlap region than does $\phi_{9j}(2p\sigma_u)$, evidently leading to more severe cancellation in the matrix element

$$\langle \phi_{9j}(1s\sigma_g) | \hat{\mu}_P(R) | \chi_{1s\sigma_g}^{(0)}(R) \rangle$$

than in

$$\langle \phi_{9j}(2p\sigma_u) | \hat{\mu}_T(R) | \chi_{2p\sigma_u}^{(0)}(R) \rangle.$$  

We find that $\sigma_L^{(2)}(2p\sigma_u)$ constitutes more than 99% of the total cross section when it is larger than $10^{-51}$ cm$^4$ s$^{-1}$, and so it would not usually be a serious approximation to neglect the channel leading to the photodissociation into the $1s\sigma_g$ continuum. Figure 8 shows the partial and the total cross sections for TPD of ($v_i = 14$, $j_i = 0$) level. As is evident, the partial cross section $\sigma_L(2p\sigma_u)$ coincides with the total cross section for almost all frequencies shown.

FIG. 8. Total and partial two-photon dissociation cross sections from the ($v_i = 14$, $j_i = 0$) level of HD$^+$ ($1s\sigma_g$). Total cross section $\sigma_L^{(2)}$. Solid curve; partial cross section $\sigma_L(2p\sigma_u)$; dashed–dotted curve; partial cross section $\sigma_L(1s\sigma_g)$; dotted curve. Note that $\sigma_L(2p\sigma_u)$ and $\sigma_L^{(2)}$ nearly coincide and cannot be distinguished in the graph.
In summary, we have extended the IDE method for the first detailed calculation of resonant TPD of HD$^+$ from vibrationally excited levels. It is hoped that these results will provide stimulus for further detailed experimental and theoretical investigations of molecular MPD processes.

ACKNOWLEDGMENTS

This work was supported in part by the Department of Energy, Division of Chemical Sciences. Acknowledgment is also made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work.

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For a recent review on nonperturbative approaches to intense field multiphoton excitation, ionization, and dissociation processes, see S.-I. Chu, Adv. At. Mol. Phys. 21, 197 (1985).


Contrary to the neutral molecule HD whose permanent dipole moment is vanishingly small, the heteronuclear molecular ion HD$^+$ has a substantial dipole moment even within the Born-Oppenheimer approximation. This is because the center of mass and center of charge in HD$^+$ are separated. The effect of nonadiabatic interactions on the dipole moment of HD$^+$ is very slight (of the order of 10$^{-3}$ times smaller). For details, see Ref. 21.

Comparisons were made with available experimental data in Refs. 3(a) and 3(b) and with theoretical data in L. Wohnericz and J. D. Poll, J. Chem. Phys. 73, 6225 (1980).

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**TABLE II. Comparison of experimental and theoretical vibration-rotation transition frequencies.**

<table>
<thead>
<tr>
<th>Transition $v_{ij} - v_{ij}$</th>
<th>Experimental frequency $^{a}$ (cm$^{-1}$)</th>
<th>Theoretical frequency $^{b}$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>17.1</td>
<td>14.0</td>
<td>1813.852</td>
</tr>
<tr>
<td>17.3</td>
<td>14.2</td>
<td>1820.200</td>
</tr>
<tr>
<td>17.5</td>
<td>14.4</td>
<td>1800.358</td>
</tr>
</tbody>
</table>

$^{a}$ Reference 3(b).

$^{b}$ This work.