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Two-photon dissociation of vibrationally excited HD⁺: The inhomogeneous differential equation approach

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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 $1s\sigma_g$ electronic state. Contrary to the H_2^+ case, where the TPD cross sections $\sigma_L^{(2)}$ 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 $\sigma_L^{(2)}$ 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 $1s\sigma_g(v_i j_i) \xrightarrow{\omega} 1s\sigma_g(v, j = j_i \pm 1)$ $\xrightarrow{\omega} 2p\sigma_u(k, j_f = j \pm 1)$ dominates the two-photon process in most of the cases we have studied. Further, the results show that $\sigma_L^{(2)}$ increases rather rapidly as the initial vibrational quantum number v_i increases, indicating that the hereronuclear 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 $\sigma_L^{(2)}$ 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.[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/cm². At these high field strengths ionization and electric breakdown of the gas would probably occur first.[2]

In contrast, MPD from high vibrational levels of diatomic molecules can be achieved efficiently as recently demonstrated experimentally.[3] Using CO and CO_2 lasers, Carrington et al.[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[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[5] like H_2^+. To circumvent this difficulty, we have recently extended the *inhomogenous differential equation* (IDE) method of Dalgarno and Lewis[6] for implicit numerical evaluation of the infinite sum over vibrational intermediate states. The method was applied[7] to two-photon dissociation (TPD) of vibrationally excited H_2^+ ($1s\sigma_g$). 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.[8]

Motivated by the recent experimental observations,[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.[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[10] using the explicit summation method of Ref. 4. They used $\mathbf{A} \cdot \mathbf{P}$ 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[7,11,12] and Raman scattering[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.

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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 ω and make a transition to a final continuum state f, dissociating in the solid angle $d\Omega_k$ with momentum $\mathbf{k}$, is given by

$$dW_{fi}^{(2)} = (M\alpha^2/\hbar)\omega^2 k\,|T_{fi}|^2 I^2\,d\Omega_k, \tag{1}$$

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

$$W_{fi}^{(2)} = \frac{M\alpha^2\omega^2 kI^2}{\hbar}\,\frac{1}{2j_i+1}\sum_{m_i}\int |T_{fi}|^2\,d\Omega_k. \tag{2}$$

$\sigma^{(2)} = W_{fi}^{(2)}/I^2$ then gives the generalized two-photon dissociation cross section.[14]

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 $1s\sigma_g$ ground electronic state and the $2p\sigma_u$ 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 $\chi_n(\mathbf{r},\mathbf{R})$, solution of either the $1s\sigma_g$ or $2p\sigma_u$ electronic state, can be written as

$$\chi_n(\mathbf{r},\mathbf{R}) = \Phi_n(\mathbf{R})\psi_n(\mathbf{r},\mathbf{R}). \tag{3}$$

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

$$\Phi_n(\mathbf{R}) = \phi_{vj}(R)\,Y_{jm}(\hat{R}). \tag{4}$$

$R\phi_{vj}(R)$ satisfies the eigenvalue equation

$$\left\{\frac{d^2}{dR^2} - \frac{j(j+1)}{R^2} + \frac{2M}{\hbar^2}\left[E_{vj} - U_n(R)\right]\right\}R\phi_{vj}(R) = 0, \tag{5}$$

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

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

$$T_{fi} = \sum_n \frac{\langle f|\mathbf{D}\cdot\boldsymbol{\epsilon}|n\rangle\langle n|\mathbf{D}\cdot\boldsymbol{\epsilon}|i\rangle}{E_n - E_i - \hbar\omega}, \tag{6}$$
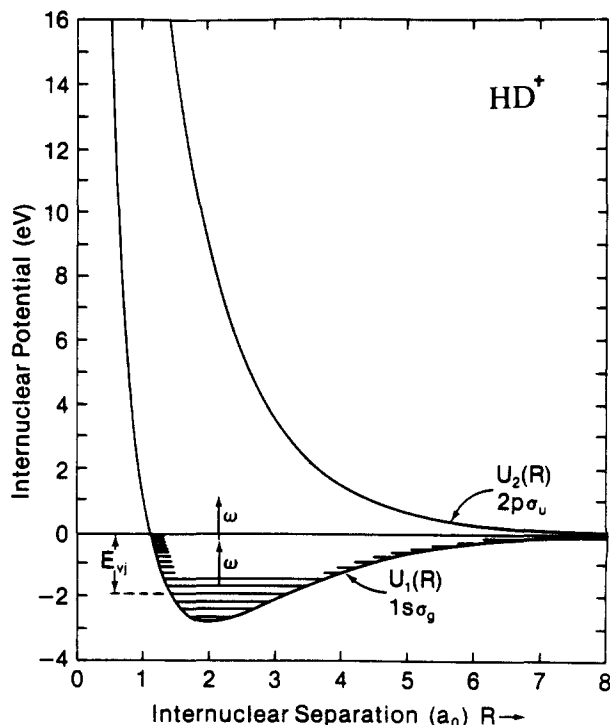

FIG. 1. Potential-energy curves for the ground electronic state ($1s\sigma_g$) and the first excited electronic state ($2p\sigma_u$) of HD⁺. Also shown is the schematic two-photon dissociation process of HD⁺.

where $\boldsymbol{\epsilon}$ is the unit polarization vector of the absorbed photons, $\mathbf{D}$ is the dipole moment operator, and the sum over n includes all bound and continuum rovibrational states $|vjm\rangle$ of the $1s\sigma_g$ electronic state and all continuum rovibrational states $|vjm\rangle$ of the $2p\sigma_u$ electronic state. The initial state $|i\rangle$ is assumed to be in a rovibrational bound state $|v_i\,j_i\,m_i\rangle$ of the $1s\sigma_g$ electronic state and the final state $|f\rangle$ can be a rovibrational continuum state of either the $1s\sigma_g$ or the $2p\sigma_u$ electronic state. The final continuum state $|f\rangle$ has the partial wave expansion

$$|f\rangle = 4\pi \sum_{j_fm_f} I^{j_f}\exp(-i\delta_{j_f})$$

$$\cdot\,\phi_{kj_f}(R)\,Y^*_{j_fm_f}(\hat{R})\,Y^*_{j_fm_f}(\hat{k})$$

$$\equiv \sum_{j_fm_f}|kj_fm_f\rangle. \tag{7}$$

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

$$T_{fi}^{(q)}(1s\sigma_g) = t_1^{(q)} + t_2^{(q)}, \tag{8a}$$

and to the $2p\sigma_u$ continuum,

$$T_{fi}^{(q)}(2p\sigma_u) = t_3^{(q)} + t_4^{(q)}. \tag{8b}$$

Here

$$t_1^{(q)} = \sum_{j_fm_f}\sum_{vjm}\frac{\langle kj_fm_f(1s\sigma)|\hat{\mu}_D C_q^{(1)}|vjm(1s\sigma)\rangle\langle vjm(1s\sigma)|\hat{\mu}_D C_q^{(1)}|v_i\,j_i\,m_i(1s\sigma)\rangle}{E_{vj} - E_{v_i j_i} - \hbar\omega}, \tag{9a}$$

$$t_2^{(q)} = \sum_{j_fm_f}\sum_{vjm}\frac{\langle kj_fm_f(1s\sigma)|\hat{\mu}_T C_q^{(1)}|vjm(2p\sigma)\rangle\langle vjm(2p\sigma)|\hat{\mu}_T C_q^{(1)}|v_i\,j_i\,m_i(1s\sigma)\rangle}{E_{vj} - E_{v_i j_i} - \hbar\omega}, \tag{9b}$$

$$t_3^{(q)} = \sum_{j_f m_f} \sum_{vjm} \frac{\langle kj_f m_f(2p\sigma)|\hat{\mu}_D C_q^{(1)}|vjm(2p\sigma)\rangle \langle vjm(2p\sigma)|\hat{\mu}_T C_q^{(1)}|v_i j_i m_i(1s\sigma)\rangle}{E_{vj} - E_{v_i j_i} - \hbar\omega},$$ (9c)

$$t_4^{(q)} = \sum_{j_f m_f} \sum_{vjm} \frac{\langle kj_f m_f(2p\sigma)|\hat{\mu}_T C_q^{(1)}|vjm(1s\sigma)\rangle \langle vjm(1s\sigma)|\hat{\mu}_D C_q^{(1)}|v_i j_i m_i(1s\sigma)\rangle}{E_{vj} - E_{v_i j_i} - \hbar\omega},$$ (9d)

where the electric dipole operator $\mathbf{D}$ has been written

$$\mathbf{D} = \hat{D}\mathbf{C}^{(1)},$$ (10)

$\mathbf{C}^{(1)}$ is the spherical tensor operator of unit rank and q is the photon polarization index. In Eq. (9), $\hat{\mu}_D(R)$ and $\mu_T(R)$ are, respectively, the permanent and the transition dipole operators given by

$$\hat{\mu}_D(R) = \langle\psi_n(\mathbf{r};\mathbf{R})|\hat{D}|\psi_n(\mathbf{r};\mathbf{R})\rangle, \quad n = 1s\sigma_g \text{ or } 2p\sigma_u,$$

and

$$\hat{\mu}_T(R) = \langle\psi_{1s\sigma_g}(\mathbf{r};\mathbf{R})|\hat{D}|\psi_{2p\sigma_u}(\mathbf{r};\mathbf{R})\rangle.$$

Owing to the dipole selection rule, only terms with $j = j_i \pm 1$ and $j_f = j \pm 1$ will contribute to the $T_{fi}^{(q)}$. Carrying out the angular integrations in Eq. (9), we find

$$t_a^{(q)} = 4\pi \sum_{j_f m_f} (-1)^{j_f} \exp(-i\delta_{j_f}) \sum_{jm} Z^{(j_f j j_i)}(m_f,q,m_i) S_a(kj_f,j,v_i j_i) Y^*_{j_f m_f}(\hat{k}), \quad a = 1,2,3,4,$$ (11)

where

$$Z^{(j_f j j_i)}(m_f,q,m_i) = \langle Y_{j_f m_f}(\hat{R})|C_q^{(1)}|Y_{jm}(\hat{R})\rangle \langle Y_{jm}(\hat{R})|C_q^{(1)}|Y_{j_i m_i}(\hat{R})\rangle,$$ (12)

and the S_a are defined by

$$S_1(kj_f,j,v_i j_i) = \sum_v \frac{\langle\phi_{kj_f}(1s\sigma)|\hat{\mu}_D|\phi_{vj}(1s\sigma)\rangle \langle\phi_{vj}(1s\sigma)|\hat{\mu}_D|\phi_{v_i j_i}(1s\sigma)\rangle}{E_{vj} - E_{v_i j_i} - \hbar\omega},$$ (13a)

$$S_2(kj_f,j,v_i j_i) = \sum_v \frac{\langle\phi_{kj_f}(1s\sigma)|\hat{\mu}_T|\phi_{vj}(2p\sigma)\rangle \langle\phi_{vj}(2p\sigma)|\hat{\mu}_T|\phi_{v_i j_i}(1s\sigma)\rangle}{E_{vj} - E_{v_i j_i} - \hbar\omega},$$ (13b)

$$S_3(kj_f,j,v_i j_i) = \sum_v \frac{\langle\phi_{kj_f}(2p\sigma)|\hat{\mu}_D|\phi_{vj}(2p\sigma)\rangle \langle\phi_{vj}(2p\sigma)|\hat{\mu}_T|\phi_{v_i j_i}(1s\sigma)\rangle}{E_{vj} - E_{v_i j_i} - \hbar\omega},$$ (13c)

and

$$S_4(kj_f,j,v_i j_i) = \sum_v \frac{\langle\phi_{kj_f}(2p\sigma)|\hat{\mu}_T|\phi_{vj}(1s\sigma)\rangle \langle\phi_{vj}(1s\sigma)|\hat{\mu}_D|\phi_{v_i j_i}(1s\sigma)\rangle}{E_{vj} - E_{v_i j_i} - \hbar\omega}.$$ (13d)

Since[15]

$$\langle Y_{jm}(\hat{R})|C_q^{(1)}|Y_{j_i m_i}(\hat{R})\rangle = (-1)^{j-m} \begin{pmatrix} j & 1 & j_i \\ -m & q & m_i \end{pmatrix} \langle j\|\mathbf{C}^{(1)}\|j_i\rangle,$$ (14)

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

$$Z^{(j_f j j_i)}(m_i,0,m_i) = (2j+1)\sqrt{(2j_i+1)(2j_f+1)} \begin{pmatrix} j_f & 1 & j \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} j & 1 & j_i \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} j_f & 1 & j \\ -m_i & 0 & m_i \end{pmatrix} \begin{pmatrix} j & 1 & j_i \\ -m_i & 0 & m_i \end{pmatrix}.$$ (15)

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 $1s\sigma_g$ continuum,

$$\sigma_q^{(v_i j_i)}(1s\sigma_g) = \frac{16M\pi^2\alpha^2\omega^2 k/\hbar}{2j_i+1} \sum_{m_i=-j_i}^{j_i} Q_1(q,m_i),$$ (16)

where $v_i j_i$ signifies the initial bound state of the $1s\sigma_g$ electronic state, and

$$Q_1(q,m_i) = Z_1^2 \cdot [S_1(kj_i+2,j_i+1,v_i j_i)$$
$$+ S_2(kj_i+2,j_i+1,v_i j_i)]^2 + \{Z_2[S_1(kj_i,j_i+1,v_i j_i) + S_2(kj_i,j_i+1,v_i j_i)]$$
$$+ Z_3[S_1(kj_i,j_i-1,v_i j_i) + S_2(kj_i,j_i-1,v_i j_i)]\}^2$$
$$+ Z_4^2[S_1(kj_i-2,j_i-1,v_i j_i) + S_2(kj_i-2,j_i-1,v_i j_i)]^2.$$ (17)

Here for convenience we have defined

$$Z_1(q,m_i) = Z^{(j_i+2,j_i+1,j_i)}(m_f,q,m_i),$$ (18a)

$$Z_2(q,m_i) = Z^{(j_i,j_i+1,j_i)}(m_f,q,m_i),$$ (18b)

$$Z_3(q,m_i) = Z^{(j_i,j_i-1,j_i)}(m_f,q,m_i),$$ (18c)

and

$$Z_4(q,m_i) = Z^{(j_i-2,j_i-1,j_i)}(m_f,q,m_i).$$ (18d)

Similarly for two-photon dissociation to the $2p\sigma_u$ continuum, we obtain

$$\sigma_q^{(v_i j_i)}(2p\sigma_u) = \frac{16M\pi^2\alpha^2\omega^2 k/\hbar}{2j_i+1}\sum_{m_i} Q_{II}(q,m_i),$$ (19)

where Q_{II} 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_i,m_i). Thus in the case of linearly polarized light $(q=0)$, for example, one finds

$$Z_1 = \left(\frac{(j_i+m_i+2)(j_i-m_i+2)(j_i+m_i+1)(j_i-m_i+1)}{(2j_i+5)(2j_i+3)^2(2j_i+1)}\right)^{1/2},$$ (20a)

$$Z_2 = \frac{(j_i+m_i+1)(j_i-m_i+1)}{(2j_i+3)(2j_i+1)},$$ (20b)

$$Z_3 = \frac{(j_i+m_i)(j_i-m_i)}{(2j_i+1)(2j_i-1)},$$ (20c)

and

$$Z_4 = \left(\frac{(j_i+m_i-1)(j_i-m_i-1)(j_i+m_i)(j_i-m_i)}{(2j_i-1)^2(2j_i-3)(2j_i+1)}\right)^{1/2}.$$ (20d)

Equations (16) and (19) show that the calculation of two-photon cross sections can be reduced to the evaluation of $S_a(kj_f j, v_i j_i)$ defined in Eq. (13). The summation over v 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

$$S_2(kj_f j, v_i j_i) = \langle\phi_{kj_f}(1s\sigma)|\hat{\mu}_T|\chi_{v_i j_i}^{(T)}\rangle,$$ (21)

and

$$S_3(kj_f j, v_i j_i) = \langle\phi_{kj_f}(2p\sigma)|\hat{\mu}_D|\chi_{v_i j_i}^{(T)}\rangle,$$ (22)

where

$$\chi_{v_i j_i}^{(T)}(R) = \sum_v \frac{\langle\phi_{vj}(2p\sigma)|\hat{\mu}_T|\phi_{v_i j_i}(1s\sigma)\rangle}{E_{vj}(2p\sigma) - E_{v_i j_i}(1s\sigma) - \hbar\omega} \cdot \phi_{vj}(2p\sigma)$$ (23)

is the well-behaved solution of the inhomogeneous differential equation

$$\left\{\frac{d^2}{dR^2} - \frac{j(j+1)}{R^2}\right.$$
$$\left. + \frac{2M}{\hbar^2}\left[E_{v_i j_i} + \hbar\omega - U_{2p\sigma_u}(R)\right]\right\}R\chi_{v_i j_i}^{(T)}(R)$$
$$= -(2M/\hbar^2)\mu_T(R)R\phi_{v_i j_i}(R).$$ (24)

Similarly S_1 and S_4 can be obtained by defining

$$\chi_{v_i j_i}^{(D)}(R) = \sum_v \frac{\langle\phi_{vj}(1s\sigma)|\hat{\mu}_D|\phi_{v_i j_i}(1s\sigma)\rangle}{E_{vj}(1s\sigma) - E_{v_i j_i}(1s\sigma) - \hbar\omega} \cdot \phi_{vj}(1s\sigma),$$ (25)

so that

$$S_1(kj_f j, v_i j_i) = \langle\phi_{kj_f}(1s\sigma)|\hat{\mu}_D|\chi_{v_i j_i}^{(D)}(R)\rangle$$ (26)

and

$$S_4(kj_f j, v_i j_i) = \langle\phi_{kj_f}(2p\sigma)|\hat{\mu}_T|\chi_{v_i j_i}^{(D)}(R)\rangle,$$ (27)

where $\chi_{v_i j_i}^{(D)}(R)$ satisfies the IDE:

$$\left\{\frac{d^2}{dR^2} - \frac{j(j+1)}{R^2}\right.$$
$$\left. + \frac{2M}{\hbar^2}\left[E_{v_i j_i} + \hbar\omega - U_{1s\sigma_g}(R)\right]\right\}R\chi_{v_i j_i}^{(D)}(R)$$
$$= -(2M/\hbar^2)\mu_D(R)R\phi_{v_i j_i}(R).$$ (28)

Equations (24) and (28) can be accurately integrated numerically for $\chi_{v_i j_i}^{(T)}(R)$ and $\chi_{v_i j_i}^{(D)}(R)$. The bound $\phi_{v_i j_i}(R)$ and continuum $\phi_{kj_f}(R)$ are also determined numerically by the Numerov method.[16] Finally $S_a(kj_f j, v_i j_i)$ 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 $\frac{1}{2}D_0 \langle \hbar\omega \langle D_0$, 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 $\mu_T(R)$ ($1s\sigma_g \leftrightarrow 2p\sigma_u$) are calculated using a two-cen-
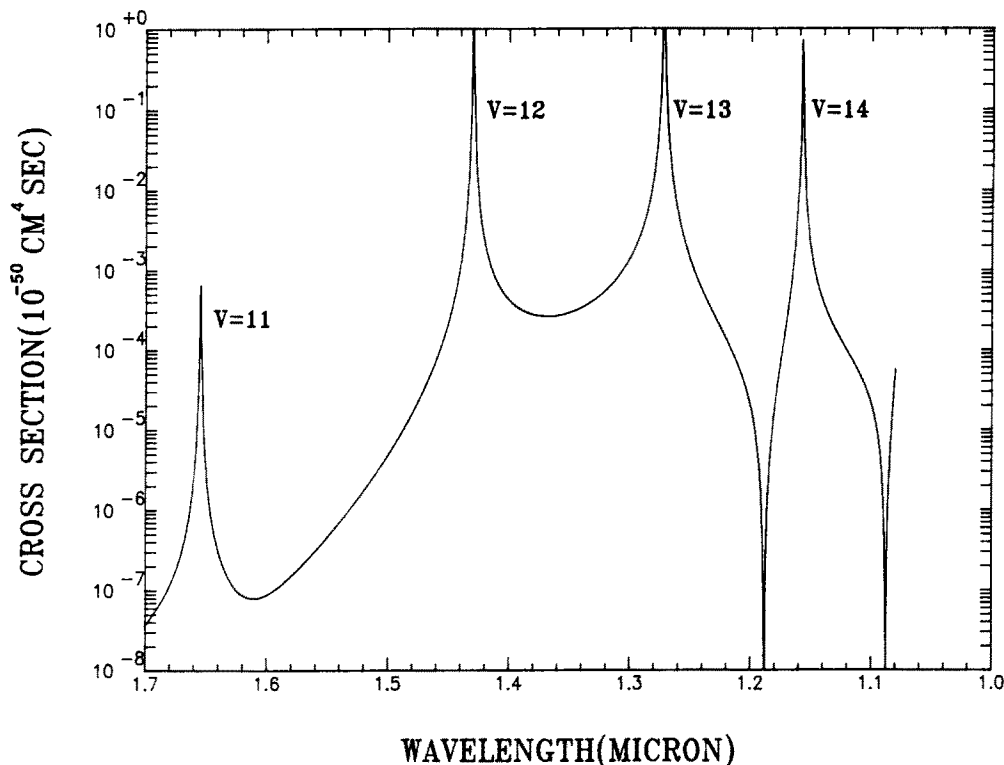
FIG. 2. Total two-photon dissociation cross section $\sigma_L^{(2)}$ from the $(v_i = 6,\ j_i = 0)$ level of the $1s\sigma_g$ electronic state of HD⁺. The vibrational quantum numbers (v) of intermediate resonance states are also indicated. All intermediate states are in the $j = 1$ rotational level, due to the dipole selection rule.

ter one-electron molecular structure code recently generated for the study of laser-induced charge-exchange processes.[18] The accuracy of the potential energy curves and the transition dipole moment is comparable to those reported by Madsen and Peek[19] and Ramaker and Peek,[20] respectively. The permanent dipole moment $\mu_D(R)$, which is the same for the $1s\sigma_g$ and $2p\sigma_u$ states in the conventional adiabatic approxi-

mation, is determined by the method described by Bunker.[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.
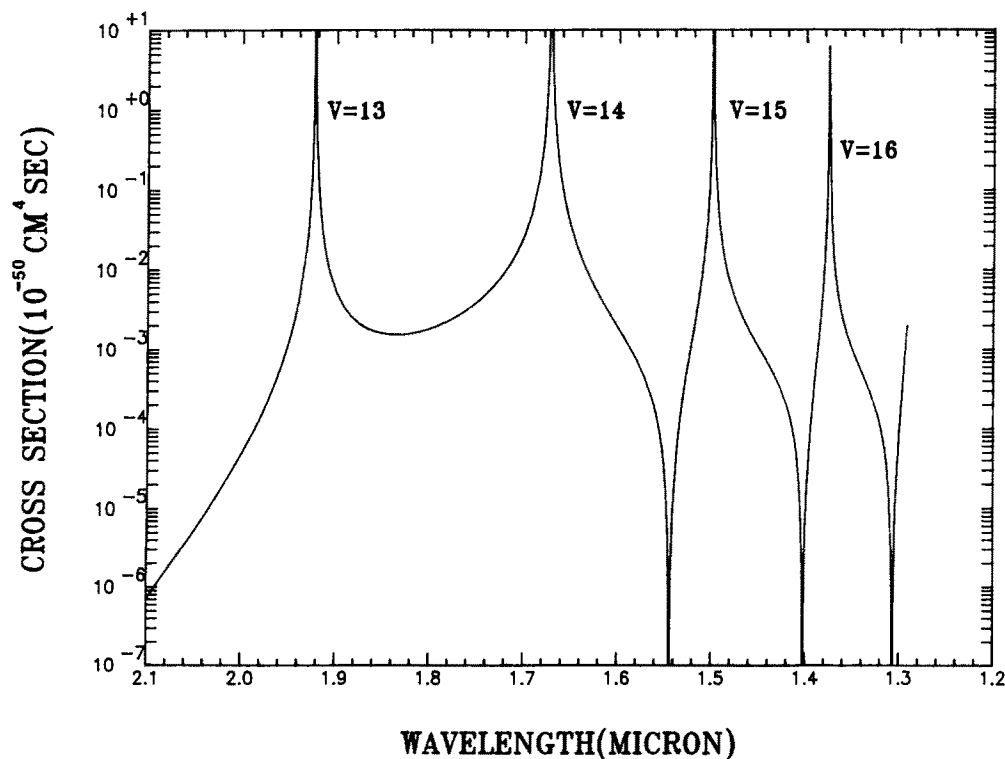

FIG. 3. $\sigma_L^{(2)}$ from the $(v_i = 8,\ j_i = 0)$ level of HD⁺ $(1s\sigma_g)$. Notation same as Fig. 2.
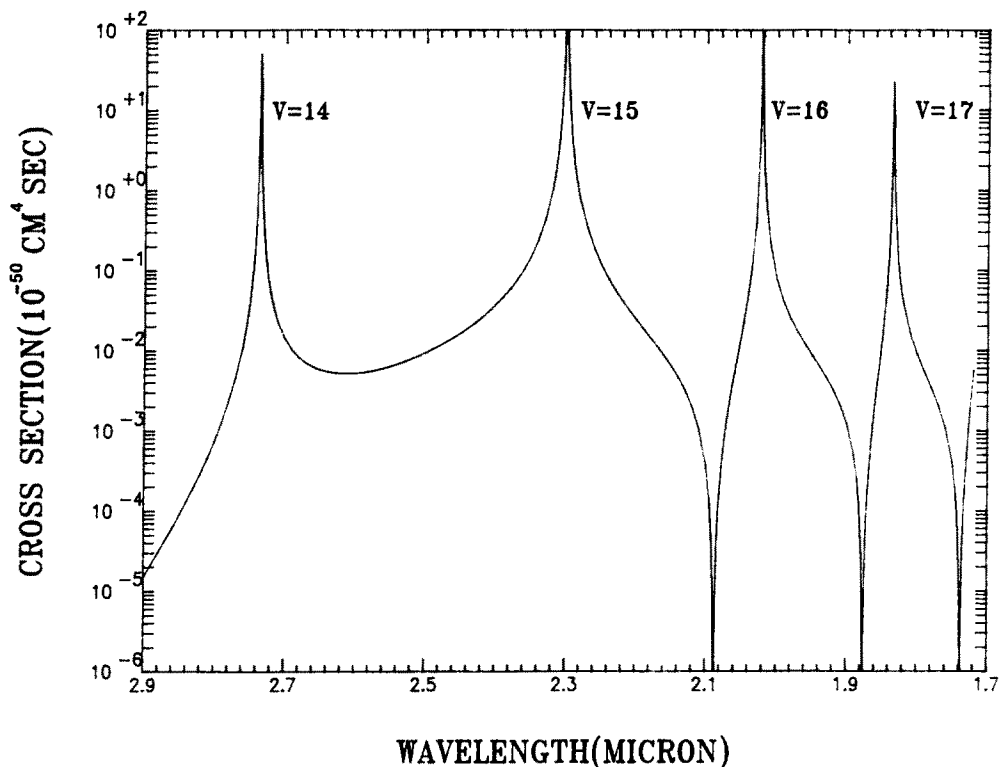
FIG. 4. $\sigma_L^{(2)}$ from the $(v_i = 10, j_i = 0)$ level of HD⁺ $(1s\sigma_g)$.

We have previously[7] presented two-photon dissociation cross sections for the vibrational levels $v_i = 6, 8, 10$, and 12 (all with $j_i = 0$) of H_2^+ $(1s\sigma_g)$. Since H_2^+ has no permanent dipole moment, $\mu_D(R) = 0$, it follows that S_2 in Eq. (13) is the only nonzero term in $\sigma^{(2)}$. As $2p\sigma_u$ is a repulsive electronic state it therefore cannot be reached from the $1s\sigma_g$ ground electronic state by absorption of a photon with ener-

gy $\hbar\omega < D_0$. Thus there are no resonances in the two-photon dissociation cross sections for H_2^+ and, in fact, it is found that $\sigma^{(2)}$ decreases monotonically as the photon energy is increased from its threshold value of $\hbar\omega = \frac{1}{2}D_0$ to $\hbar\omega = D_0$.

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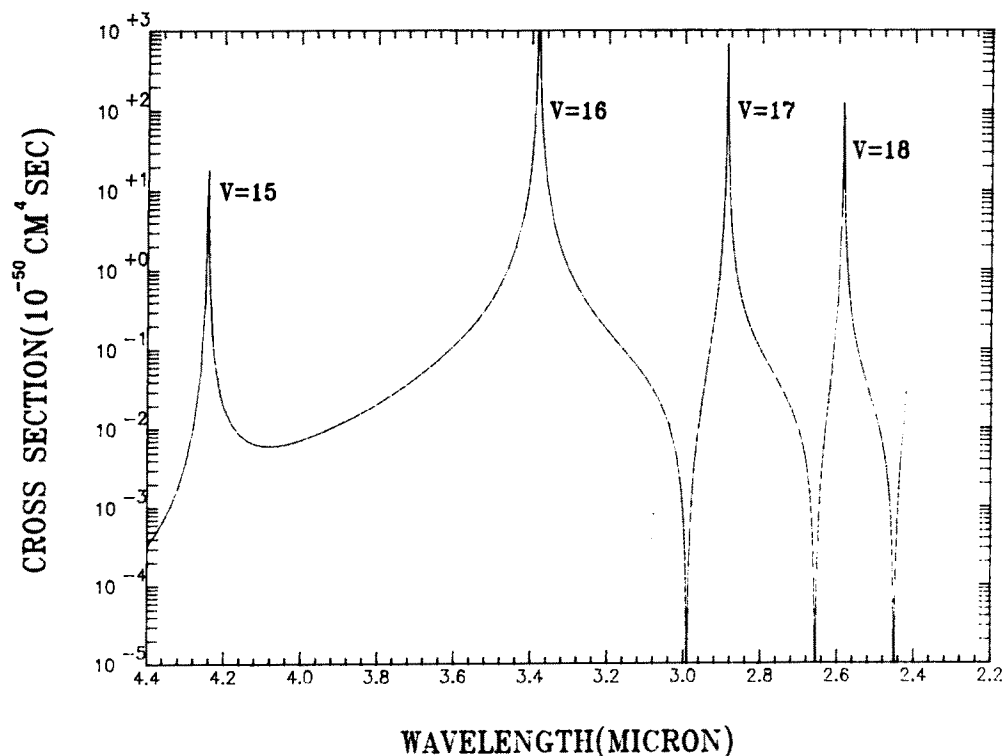

FIG. 5. $\sigma_L^{(2)}$ from the $(v_i = 12, j_i = 0)$ level of HD⁺ $(1s\sigma_g)$.
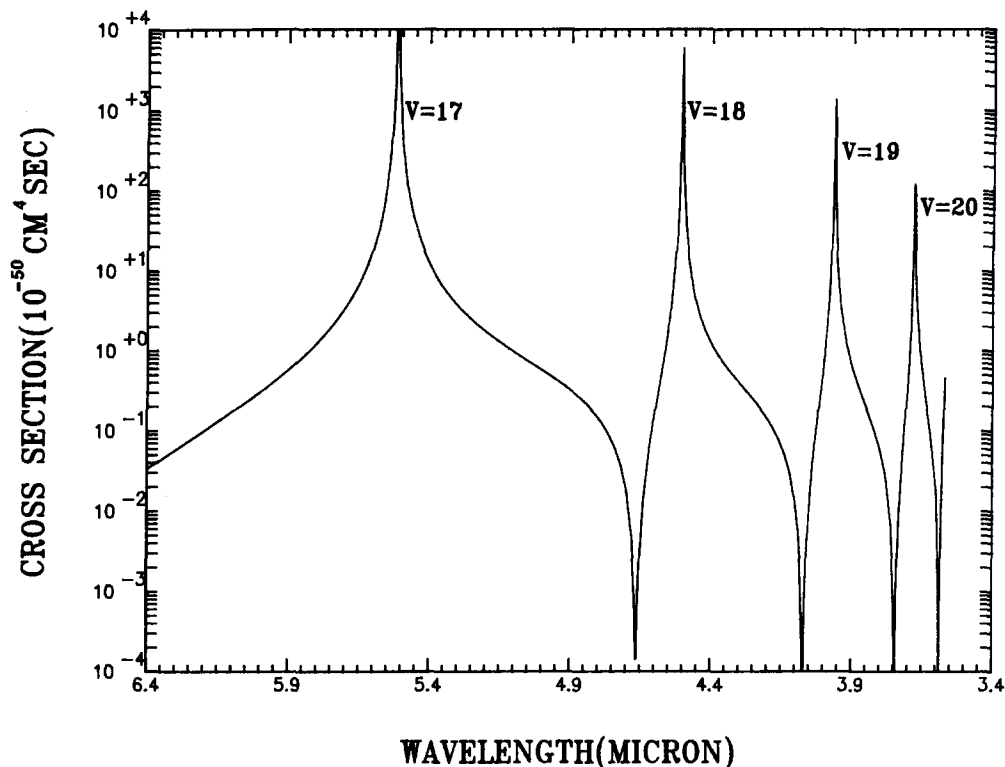
FIG. 6. $\sigma_L^{(2)}$ from the $(v_i = 14, j_i = 0)$ state of HD$^+$ $(1s\sigma_g)$.

tronic state. When the photon frequency is such that $\hbar\omega \simeq E_{vj}(1s\sigma_g) - E_{v_i j_i}(1s\sigma_g)$ 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

$$\sigma_L^{(2)}(v_i j_i) = \sigma_L^{(v_i j_i)}(1s\sigma_g) + \sigma_L^{(v_i j_i)}(2p\sigma_u)$$

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
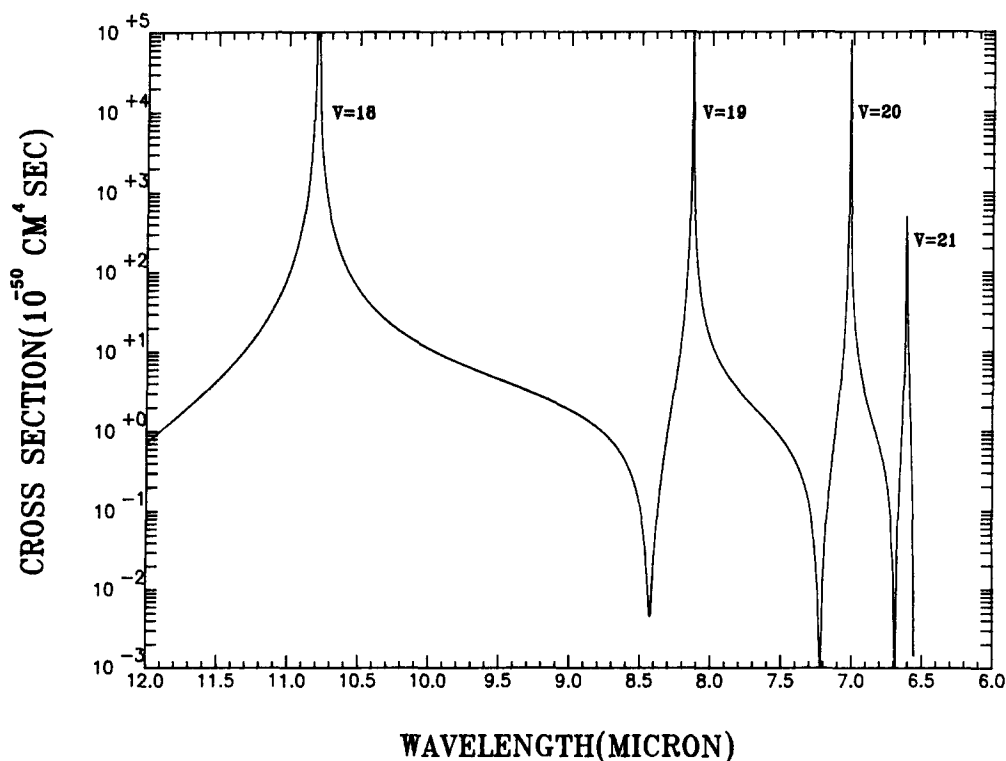

FIG. 7. $\sigma_L^{(2)}$ from the $(v_i = 16, j_i = 0)$ state of HD$^+$ $(1s\sigma_g)$.

TABLE I. An example of the relative contribution of TPD matrix elements $S_a(\lambda)$, 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 $2p\sigma_u$ continuum, respectively. Shown here is the case for the TPD: ($v_i = 14$, $j_i = 0$) $\rightarrow(v = 17, j = 1)\rightarrow(k,j_f = 0)$. The cross sections are in units of 1.0×10^{-50} cm^4 s.

$\lambda(\mu)$	S_1	S_2	S_3	S_4	$\sigma_L^{(2)}(1s\sigma_g)$	$\sigma_L^{(2)}(2p\sigma_u)$	$\sigma_L^{(2)}$
5.51[a]	$-0.382(+2)$[d]	$0.110(-1)$	$0.437(+1)$	$-0.245(+4)$	0.650	$0.267(+4)$	$0.267(+4)$
4.96[b]	$-0.730(-2)$	$0.476(-2)$	$0.905(+1)$	$-0.286(+2)$	$0.433(-8)$	0.257	0.257
4.66[c]	0.311	$0.299(-2)$	$0.124(+2)$	$-0.120(+2)$	$0.828(-4)$	$0.123(-3)$	$0.206(-3)$

[a] Near-resonance region.
[b] Off-resonance region.
[c] Interference region.
[d] $-0.382(+2) = -0.382\times10^{+2}$.

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 I shows a typical example. In general, the nonresonance terms S_2 and S_3 contribute to the smoothly varying background and to the interference region only, and $|S_3| > |S_2|$. 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 $\mu_D(R)$ and in terms of the overlap of the high-lying near-resonance intermediate vibrational levels $\phi_{vj}(1s\sigma_g)$ with the dissociating $\phi_{kj_f}(2p\sigma_u)$ and $\phi_{kj_f}(1s\sigma_g)$ continuum levels. Due to the nature of the $U_{1s\sigma_g}(R)$ and $U_{2p\sigma_u}(R)$ potential curves, $\phi_{kj_f}(1s\sigma_g)$ oscillates more rapidly in the overlap region than does $\phi_{kj_f}(2p\sigma_u)$, evidently leading to more severe cancellation in the matrix element

$$\langle \phi_{kj_f}(1s\sigma_g)|\hat{\mu}_D(R)|\chi_{v_ij_i}^{(D)}(R)\rangle$$

than in

$$\langle \phi_{kj_f}(2p\sigma_u)|\hat{\mu}_T(R)|\chi_{v_ij_i}^{(D)}(R)\rangle.$$

We find that $\sigma_L^{(v_ij_i)}(2p\sigma_u)$ constitutes more than 99% of the total cross section when it is larger than 10^{-51} cm^4 · s, 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.
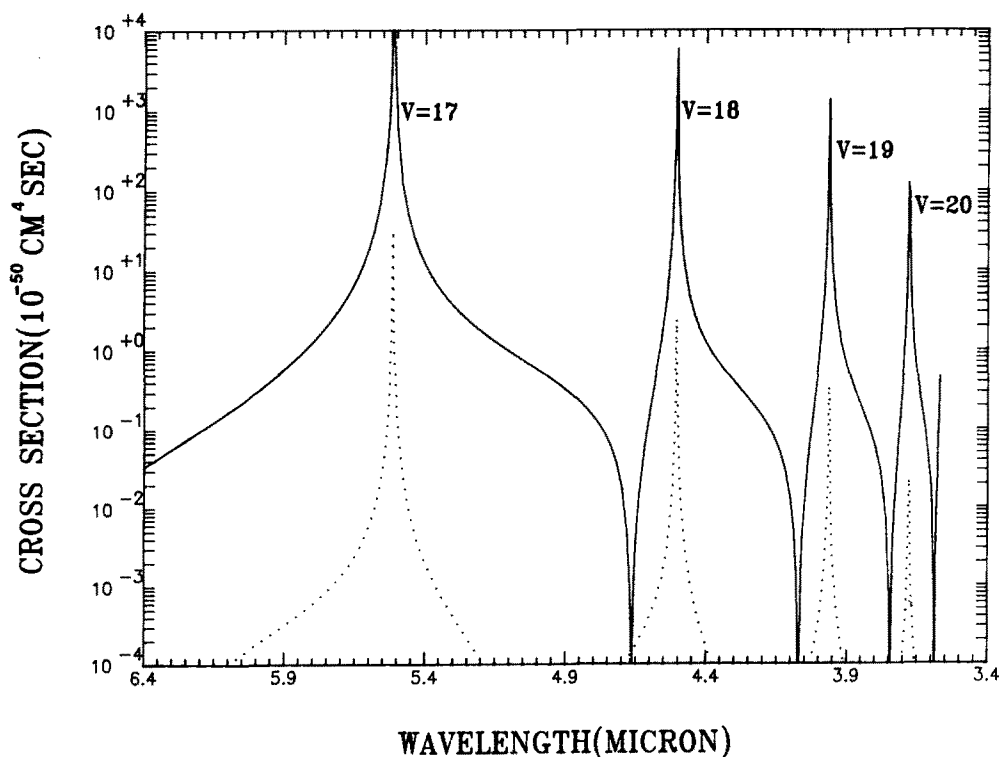

FIG. 8. Total and partial two-photon dissociation cross sections from the ($v_i = 14$, $j_i = 0$) level of HD$^+$ ($1s\sigma_g$). Total cross section $\sigma_L^{(2)}$: Solid curve; partial cross section $\sigma_L(2p\sigma_u$ continuum): dashed–dotted curve; partial cross section $\sigma_L(1s\sigma_g$ continuum): dotted curve. Note that $\sigma_L(2p\sigma_u)$ and $\sigma_L^{(2)}$ nearly coincide and cannot be distinguished in the graph.
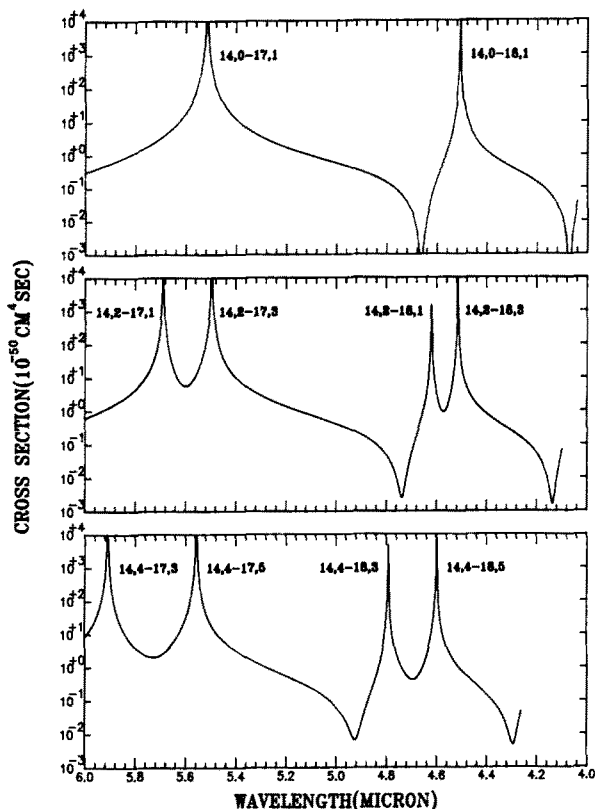
WAVELENGTH(MICRON)

FIG. 9. Total two-photon dissociation cross sections $\sigma_L^{(2)}$ from the $(v_i = 14, j_i = 0, 2, 4)$ levels of HD+ $(1s\sigma_g)$. The vibration–rotation quantum numbers for the initial and intermediate resonance states $(v_i j_i \rightarrow vj)$ are indicated. Note the resonance positions depend strongly on the initial rotational quantum number j_i.

In Fig. 9 we present the total cross sections for the $v_i = 14$ level of HD+ as a function of the initial rotational quantum number j_i. Only a portion of the cross sections in the neighborhood of the $v = 17$ and 18 resonances is shown. For $j_i > 0$, there are two resonance channels ($j = j_i \pm 1$) for each intermediate vibrational quantum number v. We note that while the resonance line shapes are qualitatively similar, the resonance positions may change considerably as j_i varies.

Finally, as a measure of the accuracy of the predicted resonance transition frequencies we show in Table II some representative comparisons of the predicted and experimental frequencies. We find virtually all resonance peaks presented in Figs. 2 to 9 are located within 1 cm^{-1} of their corrected positions.[23]

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

Transition $vj \leftarrow v_i, j_i$		Experimental frequency[a] (cm^{-1})	Theoretical frequency[b] (cm^{-1})
17,1	14,0	1813.852	1813.06
17,3	14,2	1820.200	1819.40
17,5	14,4	1800.358	1799.52

[a] Reference 3(b).
[b] This work.

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

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