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# Stieltjes-imaging calculations of photodissociation

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The applicability of Stieltjes-imaging techniques to calculations of molecular photodissociation cross sections is explored. Detailed comparisons for the diatomic molecules LiH and H<sub>2</sub> are made which suggest that reasonable accuracy can be obtained with moderate basis sets. The methods are used to predict the photodissociation cross sections for absorption from low-lying vibrational levels of H<sub>3</sub><sup>+</sup>.

## I. INTRODUCTION

Stieltjes imaging is a technique by which continuous distributions can be approximated by discrete representations. Stieltjes imaging techniques have been widely used in calculations of photodetachment and photoionization cross sections of atomic and molecular systems<sup>1,2</sup> but appear not to have been exploited in studies of molecular photodissociation. They may have a particular utility in considerations of the photodissociation of polyatomic systems in those instances where detailed information on the dissociation products is not required. Here we assess the method by applying it to the diatomic systems H<sub>2</sub> and LiH and the triatomic system H<sub>3</sub><sup>+</sup> for which photodissociation cross sections have been obtained by other procedures.

## II. THEORY

Suppose **R** denotes collectively the position vectors of the nuclei and **r** those of the electrons of the molecular system. We assume that the electron and nuclear motions can be separated and that photodissociation occurs by a transition from an initial discrete vibrational level with eigenfunction  $X_{v''}(\mathbf{R})$  associated with a particular electronic state to a final continuum vibrational level with eigenfunction  $X_{v'}(\mathbf{R})$  associated with a different electronic state. The dipole moment of the transition connecting the electronic states we write as  $D(\mathbf{R})$ .

Detailed presentations of the theory of photodissociation have been given by Heller<sup>3</sup> using a time-dependent formulation and by Band, Freed, and Kouri<sup>4</sup> using a steady-state description. In the steady-state description, the cross section  $\sigma_{v''}(E)$  for the absorption of a photon of energy  $E$  may be written in terms of the differential oscillator strength  $df_{v''}/dE_{v'}$  according to

$$\sigma_{v''}(E) = 4.03 \times 10^{-18} \frac{df_{v''}}{dE_{v'}} \text{ cm}^2, \quad (1)$$

where  $E_{v'}$  is the kinetic energy of the dissociation products in atomic units.

Stieltjes imaging is a procedure by which the continuum oscillator strength  $df_{v''}/dE_{v'}$  may be obtained from a distribution of discrete pseudo-oscillator strengths

$$g_{v''n} = \frac{2}{3} (E_n - E_{v''}) | \langle X_{v''}(\mathbf{R}) | D(\mathbf{R}) | \psi_n(\mathbf{R}) \rangle |^2,$$

calculated with a finite basis set of functions  $\psi_n(\mathbf{R})$  with respect to which the Hamiltonian  $H'$  governing the nuclear motion in the final state is diagonal:

$$\langle \psi_n(\mathbf{R}) | H' | \psi_m(\mathbf{R}) \rangle = E_n \delta_{nm}.$$

Various methods are available to derive  $df_{v''}/dE_{v'}$  from the moments

$$S_{-k} = \sum_n (E_n - E_{v''})^{-k} g_{v''n}.$$

We found that the Stieltjes-Tchebycheff densities<sup>1,2</sup> provided the smoothest values of  $df_{v''}/dE_{v'}$  and the cross sections we report were obtained using representations of order up to ten.

We chose to represent  $\psi_n(\mathbf{R})$  by superpositions of harmonic oscillator wave functions  $\phi_s(\mathbf{R})$ . Other more flexible choices are possible<sup>5,6</sup> but harmonic oscillator functions offer considerable analytical simplifications and with them we were able to accommodate larger basis sets. Lin and Drake<sup>7</sup> have argued that a harmonic oscillator basis set provides a compact representation of the bound and continuum vibrational states of an anharmonic oscillator in the inner region and Lin<sup>8</sup> and Caldwell and Gordon<sup>9</sup> have shown that they can produce reliable discrete Franck-Condon factors.

For a diatomic molecule  $D(\mathbf{R}) = D(R)$ . We may ignore orientation effects and use purely radial functions

$$\phi_s(R) = \left\{ \left( \frac{\alpha}{\pi} \right)^{1/2} \frac{1}{2^s s!} \right\}^{1/2} H_s(\zeta) \exp(-\zeta^2/2),$$

where  $R$  is the internuclear distance,  $\zeta = \alpha^{1/2}(R - R_0)$ , and  $H_s(\zeta)$  is an Hermite polynomial. For computational convenience in the calculation of the pseudo-oscillator strengths, we adopted the same basis set to represent the initial vibrational wave function  $X_{v''}(\mathbf{R})$ :

$$X_{v''}(\mathbf{R}) = \sum_s a_s^{v''} \phi_s(\mathbf{R}).$$

The coefficients  $a_s^{v''}$  were determined by diagonalizing the Hamiltonian governing the nuclear motion in the initial state. Any defects in the representations caused by the adoption of the same values of  $\alpha$  and  $R_0$  for the initial and final states can be overcome by increasing the size of the basis sets.<sup>8</sup> Basis sets large enough to reproduce the bound energy levels of the initial and final states provided sufficient continuum eigenvalues to yield converged cross sections using the Stieltjes techniques.

If for simplicity we ignore the centrifugal repulsion,

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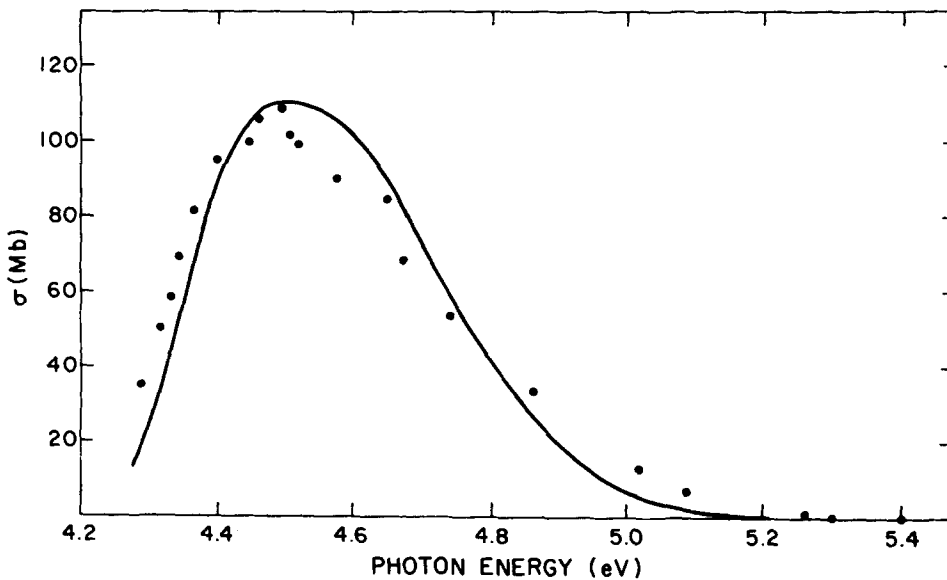


FIG. 1. The photodissociation cross sections of the  $v''=0$  level of the  $X^1\Sigma^+$  state of LiH by absorption into the  $B^1\Pi$  state. The full line represents conventional calculations (Ref. 12) and the dots denote the Stieltjes imaging values.

the initial and final Hamiltonians have the radial form

$$H = -\frac{\hbar^2}{2M} \frac{d^2}{dR^2} + V(R),$$

where  $M$  is the reduced mass and  $V(R)$  is the potential energy in the initial or final state. The matrix elements of the kinetic energy operator may be obtained analytically and are given by the formula

$$\left\langle s' \left| \frac{d^2}{dR^2} \right| s \right\rangle = -\alpha \left(s + \frac{1}{2}\right) \delta_{s,s'} + \frac{\alpha}{2} \{ [s(s-1)]^{1/2} \delta_{s',s-2} + [(s+1)(s+2)]^{1/2} \delta_{s',s+2} \}.$$

Those of the potential energy were obtained following a procedure suggested by Harris, Engerholm, and Gwinn<sup>10</sup> in which the matrix  $R$  with elements

$$R'_{ss} = \langle \phi_s | R | \phi_s \rangle$$

is diagonalized by a similarity transformation  $U$  to yield eigenvalues

$$R_s = (U^{-1} R U)_{ss}.$$

Then the matrix of  $V$  is given by

$$V = UV(R_s)U^{-1}.$$

The matrix elements of the dipole moment  $D(R)$  may be evaluated in similar fashion.

For the triatomic system  $H_3^+$ , we employed the initial and final state Hamiltonians of Kulander and Bottcher<sup>11</sup> which are expressed as functions of the distance  $x$  between one hydrogen nucleus and the center of mass of the other two and the distance  $y$  between the pair of hydrogen nuclei. The basis set consisted of products of harmonic oscillator functions  $\phi_s(x)\phi_{s'}(y)$ . The initial nuclear eigenfunction  $X_i(x, y)$  was written as a superposition.

$$X_i(x, y) = \sum_{s,s'} a_{ss'}^i \phi_s(x) \phi_{s'}(y),$$

and the coefficients  $a_{ss'}^i$  were obtained by diagonalizing

the initial state Hamiltonian. The discrete representation of the final state was obtained by diagonalizing the final state Hamiltonian.

### III. CALCULATIONS

#### A. LiH

Accurate values of the photodissociation cross section of LiH arising from absorption in the transition from the ground  $X^1\Sigma^+$  state to the excited  $B^1\Pi$  state have been obtained by Kirby and Dalgarno<sup>12</sup> using the interaction potentials of Way and Stwalley,<sup>13</sup> Stwalley *et al.*,<sup>14</sup> and the transition dipole moment of Docken and Hinze.<sup>15</sup>

Experimentally,<sup>13-15</sup> three vibrational levels have been found for the  $B^1\Pi$  state of LiH. Our adopted potential has a shallow minimum which contains two vibrational levels. For a sufficiently large basis set, the vibrational level energies in the initial state are in good agreement with the exact energies. With a basis set of 70 functions, the energies of the low-lying vibrational levels are stable for  $\alpha$  and  $R_0$  in the ranges  $4.5 < \alpha < 6.5$  and  $5.5 < R_0 < 7$  for the ground state and in the ranges  $3 < \alpha < 7$  and  $4 < R_0 < 8$  for the excited state. Within these ranges, the photodissociation cross sections derived from representations of order five up to ten had apparently converged. Figure 1 presents the cross sections derived for  $v''=0$  from the basis set with  $\alpha=6$  and  $R_0=7$ , a choice of parameters which is common to the regions of stability of both the ground and excited states. The cross sections calculated by Kirby and Dalgarno<sup>12</sup> with conventional methods are shown as the full line in Fig. 1. The Stieltjes-imaging cross section points group around the accurate curve.

The harmonic oscillator representation allows us to produce with little additional effort cross sections for absorption from excited vibrational levels and Fig. 2 shows the Stieltjes cross section data for the transition from the  $v''=1$  vibrational level of the  $X^1\Sigma^+$  state of LiH into the  $B^1\Pi$  continuum.

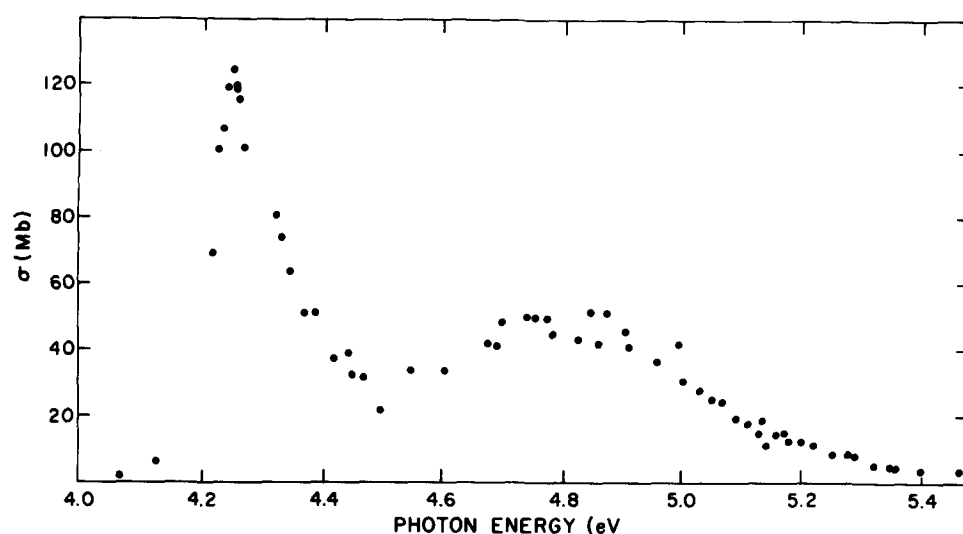


FIG. 2. Stieltjes imaging photodissociation cross section for the  $v''=1$  level of the  $X^1\Sigma^+$  state of LiH by absorption into the  $B^1\Pi$  state.

## B. $H_2$

The  $X^1\Sigma_g^+-B^1\Sigma_u^+$  transition in  $H_2$  is of a different character from the  $X^1\Sigma^+-B^1\Pi$  transition in LiH. The  $B^1\Sigma_u^+$  state of  $H_2$  has a deep well containing 36 vibrational levels, which must be largely incorporated into the basis set if the vibrational continuum is to be adequately represented by the high-lying eigenvectors.

The utility of a harmonic oscillator basis for the calculation of the Franck-Condon factors of the  $X^1\Sigma_g^+-B^1\Sigma_u^+$  transition in  $H_2$  has been demonstrated by Lin<sup>8</sup> and Caldwell and Gordon<sup>9</sup>. We present in Table I discrete absorption oscillator strengths  $f_{v',v''}$  for  $v''=0, 1, 5$ , and 10 and selected values of  $v' \leq 24$  calculated with a 70-term basis set with  $\alpha=9.5$  and  $R_0=4.0$ . The interaction potentials  $V(R)$  and the dipole moment function  $D(R)$  were adopted from the conventional calculations of Allison and Dalgarno<sup>16</sup> whose results for  $f_{v',v''}$  are included in the table. The accuracy achieved by the harmonic oscillator basis set is high. It becomes inadequate for higher values of  $v''$  and  $v'$ . The loss of accuracy can be remedied by choosing  $\alpha$  and  $R_0$  to optimize the higher

energy levels and by increasing the size of the basis set.

The photodissociation cross sections obtained from basis sets of 70 and 90 functions are compared in Figs. 3-5 for initial vibrational levels  $v''=0, 1$ , and 5. Apart from the threshold regions where discrepancies persist, the Stieltjes imaging values reproduce closely the correct cross sections<sup>18</sup> for  $v''=0$  and  $v''=1$ . The description of the threshold region could be improved by adding any available information on the location of the threshold and on the shape of the cross section,<sup>17</sup> or alternatively, by regarding it as the extension of the discrete oscillator strength distribution  $f_{v',v''} dv'/dE_{v'}$ <sup>18</sup> whose convergence can be assessed by inspection. For  $v''=5$  the cross section maximum is reproduced in location and in magnitude but there is a loss of accuracy at high and low photon energies. The nodal structure of the initial state eigenvector causes cancellation in the evaluation of the matrix element and a more refined analysis of the moment distribution appears to be necessary to obtain reliable cross sections for absorption by high-lying vibrational states.

TABLE I. Absorption oscillator strengths  $f_{v',v''}$  of the  $X^1\Sigma_g^+-B^1\Sigma_u^+$  transition in  $H_2$ .

$v'/v''$	$(f_{v',v''} \times 10^2)$							
	0		1		5		10	
	a	b	a	b	a	b	a	b
0	0.17	0.17	1.28	1.29	11.66	11.65	0.00	0.00
4	2.25	2.25	3.37	3.37	0.12	0.12	1.25	1.24
8	2.52	2.52	0.08	0.08	0.24	0.23	2.33	2.33
12	1.50	1.50	0.48	0.49	1.28	1.28	1.37	1.37
16	0.72	0.72	0.89	0.89	0.10	0.10	0.19	0.19
20	0.40	0.32	0.96	0.75	0.40	0.25	0.54	0.50
24	0.17	0.15	0.70	0.49	0.73	0.48	0.44	0.00

<sup>a</sup>70-term harmonic oscillator basis.

<sup>b</sup>Exact (Ref. 16).

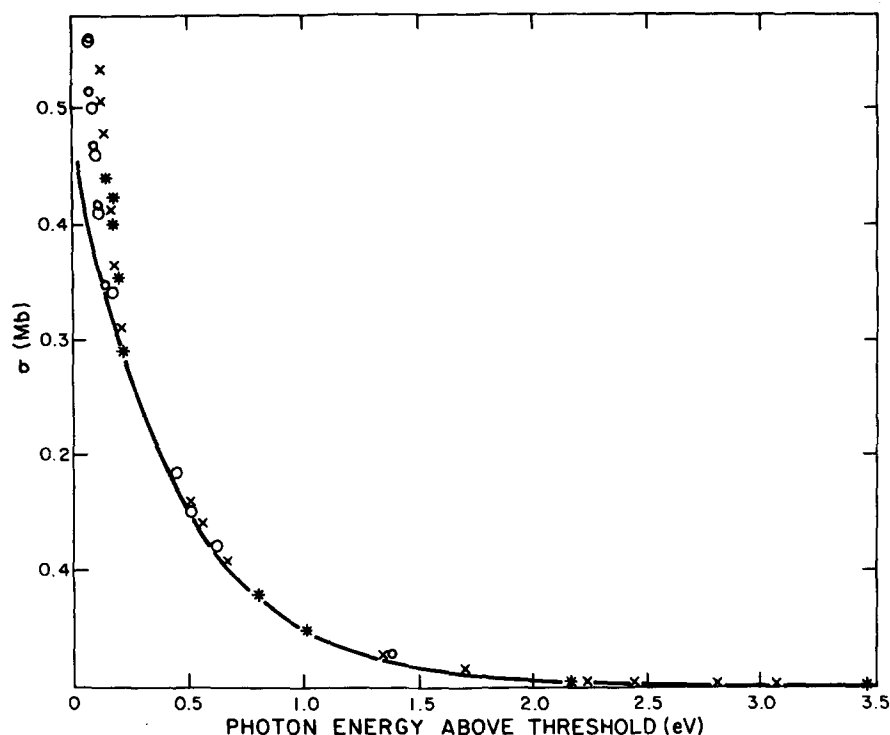


FIG. 3. The photodissociation cross sections of the  $\nu''=0$  level of the  $X^1\Sigma_g^+$  state of  $H_2$  by absorption into the  $B^1\Pi_u$  state. The full line represents conventional calculations and the symbols are Stieltjes imaging values for various orders and basis sets.

### C. $H_3^+$

Although the Stieltjes imaging technique is convenient for application to diatomic molecules it does not compete in accuracy with alternative procedures. For polyatomic molecules where the characterization of the final state presents formidable practical difficulties, Stieltjes imaging may provide a superior physical description of the initial absorption process.

As an example we explore the photodissociation of  $H_3^+$ .

TABLE II. Vibrational eigenvalues  $E_n$  and level spacings  $\Delta E_n = E_n - E_1$  for the ground state of  $H_3^+$  in  $\text{cm}^{-1}$ .

$n$	$E_n$		$\Delta E_n$	
	Ref. 11	This paper	Ref. 11	This paper
1	-75 104	-75 093	0	0
2	-72 865	-72 863	2 239	2 228
3	-71 724	-71 710	3 380	3 383
4	-70 736	-70 758	4 368	4 335
5	-69 595	-69 610	5 509	5 483
6	-68 651	-68 794	6 453	6 299
7	-68 410	-68 416	6 694	6 677
8	-67 576	-67 628	7 520	7 465
9	-66 523	-66 995	8 582	8 098
10	-66 435	-66 460	8 669	8 633
11	-65 557	-65 797	9 547	9 206
12	-65 206	-65 391	9 898	9 702
13	064 525	-65 216	10 579	9 877
14	-64 262	-64 618	10 842	10 475
15	-63 450	-64 274	11 654	10 819
16	-63 362	-63 919	11 742	11 174
17		-63 426		11 667
18		-63 108		11 985
19		-62 889		12 204
20		-62 418		12 675

We adopt the model of Kulander and Bottcher<sup>11</sup> in which the hydrogen atoms are constrained to isosceles triangular configurations and overall rotations are ignored. Absorption occurs to excited electronic states which we designate by numerals 2 and 3. As the distance between one hydrogen nucleus and the center of mass of the other pair increases, state 2 separates to H and  $H_2^+(^2\Sigma_u^+)$  and state 3 to H and  $H_2^+(^2\Sigma_u^-)$ . The  $^2\Sigma_u^+$  state may be vibrationally excited or dissociated. The  $^2\Sigma_u^-$  state is repulsive and dissociation occurs.

We calculated the potential energy surfaces of the ground and excited states following the procedures of

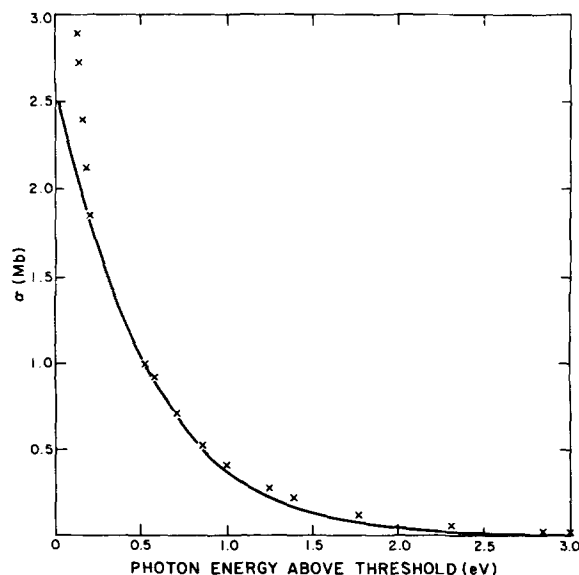


FIG. 4. As for Fig. 3 for the  $\nu''=1$  level.

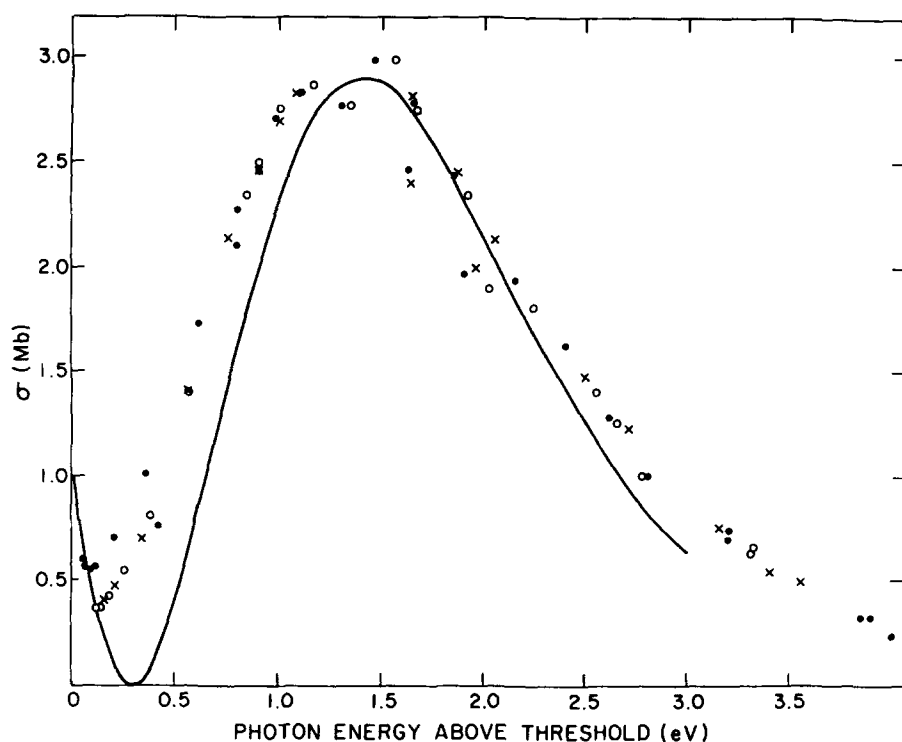


FIG. 5. As for Fig. 3 for the  $v''=5$  level.

Kulander and Bottcher.<sup>11</sup> With the parameter values  $\alpha=10.13$  and  $R_0=1.7235$  in a harmonic oscillator product basis set of size  $20 \times 20$ , we obtained 133 bound vibrational levels in the  $H_2^+$  ground state. The energies of the low-lying levels measured from the fully dissociated system are presented in Table II where they are compared with the calculations of Kulander and Bottcher.<sup>11</sup> Despite the small size of our basis set, all levels other than the first lie below those of Kulander and Bottcher<sup>11</sup> and our calculations are presumably more accurate. (Other calculations of greater accuracy have been carried out with improved potential energy surfaces<sup>19</sup> and measurements have been performed.<sup>20</sup>)

To calculate the absorption cross sections we adopted

the analytical representation of  $D(R)=D(x,y)$  used by Kulander and Heller.<sup>21</sup> The Stieltjes-imaging values of the cross sections for absorption by the lowest vibrational level into state 3 derived from representations of order up to eight are illustrated in Fig. 6 which includes the cross sections obtained by Kulander and Heller<sup>21</sup> from a time-dependent theory of photodissociation.

For the low order representation, the cross sections appear to contain an oscillatory structure in the region between 20 and 24 eV, which persists with increase in basis size. We have explored the use of the Stieltjes technique in a model calculation in which the moments were derived from an assumed cross section and it seems likely that the structure is an artifact of the

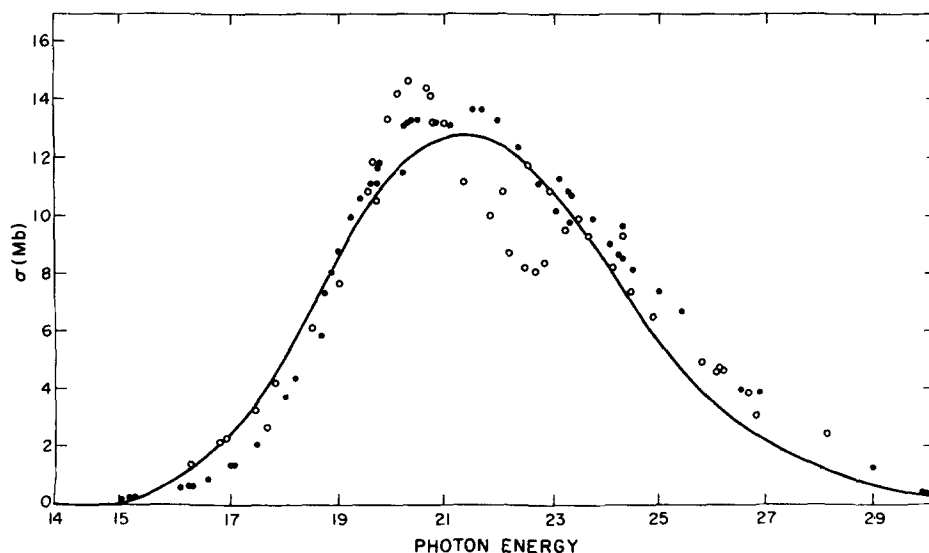


FIG. 6. Absorption cross sections for the lowest vibrational level of  $H_2^+$  into the dissociative state 3. The full line reproduces the calculations of Kulander and Heller.(Ref. 21). The symbols are Stieltjes imaging values for various orders. (Lower order points are indicated by open circles.)

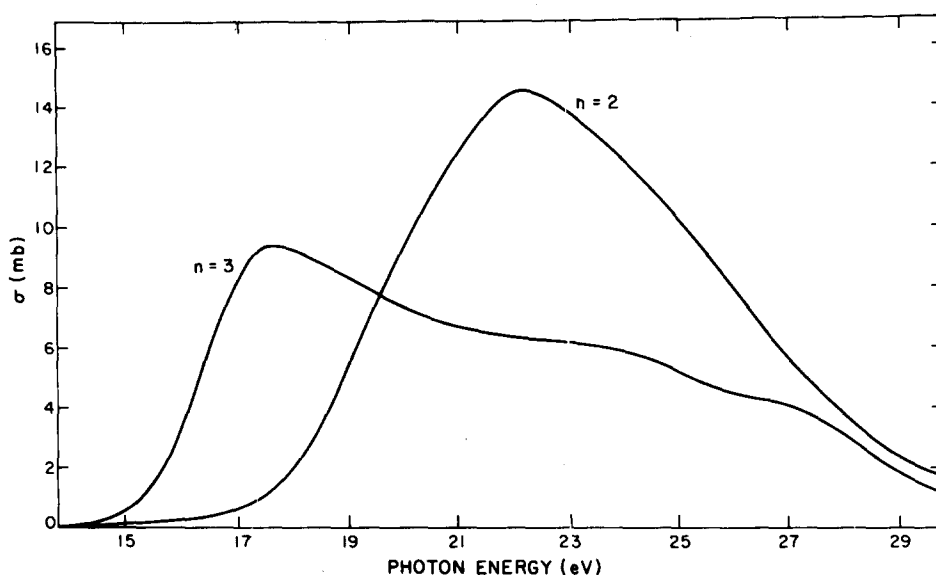


FIG. 7. Smoothed Stieltjes imaging cross sections for absorption out of the first,  $n=2$ , and second,  $n=3$ , excited vibrational levels of  $H_3^+$  into the excited dissociative state 3.

imaging procedure. The cross sections derived from higher orders do not oscillate and agree satisfactorily with those calculated by Kulander and Heller.<sup>21</sup>

The cross sections for absorption from other bound states of  $H_3^+$  are readily obtained from the calculation for the ground state. Figure 7 shows the Stieltjes imaging cross sections for absorption into state 3 from the first and second excited vibrational levels.

The potential energy surface of state 2 of  $H_3^+$  accommodates discrete vibrational levels of  $H_2^+$  and continuum hydrogen atoms which are represented in the diagonalized basis set by eigenfunctions with negative eigenvalues measured with respect to the three particle dissociation. In evaluating the continuum contributions to the moments  $S_{\alpha\beta}$ , we included these negative energy states. The absorption cross sections obtained from the imaging process were correct qualitatively in shape and position but results from a  $20 \times 20$  basis set had not converged. The potential energy surface of state 2 is highly asymmetric in the  $x$  and  $y$  coordinates and our use of a product basis of harmonic oscillator functions with the same parameters is a severe limitation. To obtain accurate cross sections additional flexibility is required, either by allowing different choices of  $\alpha$  and  $R_0$  in the harmonic oscillator functions forming the products or by employing more elaborate functions in the basis set.

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