

Cross sections for rotational excitations of NH_3 , PH_3 , AsH_3 , and SbH_3 by electron impact

Márcio T. do N. Varella

Instituto de Física Gleb Wataghin, Universidade Estadual de Campinas, UNICAMP 13083-970, Campinas, São Paulo, Brazil

Márcio H. F. Bettega

Departamento de Física, Universidade Federal do Paraná, UFPR, Caixa Postal 19081, 81531-990 Curitiba, Paraná, Brazil

Antônio J. R. da Silva

Instituto de Física, Universidade Estadual de São Paulo, USP, Caixa Postal 66318, 05389-970, São Paulo, São Paulo, Brazil

Marco A. P. Lima

Instituto de Física Gleb Wataghin, Universidade Estadual de Campinas, UNICAMP 13083-970, Campinas, São Paulo, Brazil

(Received 27 March 1998; accepted 29 October 1998)

We report elastic and rotationally inelastic cross sections for $e^- - \text{XH}_3$ collisions (X: N, P, As, Sb) at the static-exchange level of approximation. The energy range was from 7.5 up to 30 eV. Our fixed-nuclei scattering amplitudes were obtained through the Schwinger multichannel method with pseudopotentials (SMCPP) [M. H. F. Bettega, L. G. Ferreira, and M. A. P. Lima, *Phys. Rev. A* **47**, 1111 (1993)]. The rotational cross sections were obtained with the help of the adiabatic-nuclei-rotation approximation. There is good agreement with available experimental elastic cross sections. In order to improve rotational cross sections at small scattering angles for the dipole-allowed $00 \rightarrow 10$ rotational excitation, we have combined the SMCPP and the first Born approximation of the full interaction potential and also of the dipole moment potential. To our knowledge this is the first time that rotational excitation cross sections for these molecules are reported. © 1999 American Institute of Physics. [S0021-9606(99)02005-X]

I. INTRODUCTION

The excitation of molecular targets by low-energy electrons is an important energy-loss mechanism in molecular gases, playing a relevant role in determining the electron-velocity distribution in a gaseous discharge, in electron drift experiments, and in the ionospheres of the Earth and other planets.¹ Focusing on technological applications in which scattering of slow electrons by molecules is of crucial importance, one may cite the description of cold plasma²⁻⁴ and laser development and modeling.⁵

In particular, pure rotational energy transfer from electrons to molecular gases in slow collisions is often quite effective. As a result, either in gas discharges or in the ionosphere of the Earth, a considerable fraction of the total energy of the free-electron gas is transferred to the rotational energy of molecules.⁶ In spite of such importance, there are very few calculations of rotationally resolved cross sections for polyatomic targets available in the literature. In fact, to our knowledge, there are no rotationally resolved cross sections reported for PH_3 , AsH_3 and SbH_3 . On the other hand, many works have tried to deal with rotational excitations of NH_3 , starting with the early effort of Altshuler.⁷ Most of such attempts, however, have been limited to the first Born level of approximation. We could find only two papers where more sophisticated approaches have been applied: Jain and Thompson⁸ have reported rotationally resolved momen-

tum transfer cross sections (MTCS), whereas Gianturco⁹ also has reported MTCS and integral cross sections (ICS). Differential cross sections (DCS) were found only for the rotationally elastic transition ($J=0K=0 \rightarrow J'=0K'=0$) and for rotationally summed DCS.⁹ Unfortunately, the experimental situation is even worse, and we could not find reported data for rotational excitations of XH_3 (X: N, P, As, Sb), which is the object of the present investigation.

Theoretical works are mainly restricted by computational limitations due to the large number of electrons of polyatomic targets. On the other hand, experimental efforts face the problem of insufficient resolution of measurement devices, since the rotational levels of polyatomic molecules are very close to each other. For the molecular targets treated in this work, typical separations are 10^{-4} – 10^{-3} eV. There are, however, available rotationally resolved experimental data for CH_4 ¹⁰ and H_2O ,⁶ which have typical separations between neighboring rotational levels of 10^{-4} and 10^{-3} eV, respectively. Those measurements took advantage of a broadening, caused by pure rotational excitations, of energy-loss peaks. The broadened peaks were then rotationally resolved based on theoretical expressions (high- J approximation for the water molecule,¹¹ and a cross section formula of Shimamura¹² for methane). Since the ammonia molecule has a typical separation between neighboring rotational levels around 10^{-3} eV, we believe that the procedure applied for

methane and water could be extended to NH_3 , therefore leading to rotationally resolved cross sections for this system. We outline in Appendix A the procedure to perform such a task.

Recently, we applied the Schwinger multichannel method with pseudopotentials (SMCPP), combined with the adiabatic-nuclei-rotation (ANR) approximation, to calculate rotational excitation cross sections for T_d symmetry-point-group molecules, such as XH_4 (X: C, Si, Ge, Sn, Pb),¹³ CX_4 (X: F, Cl) and SiY_4 (Y: Cl, Br, I).¹⁴ In the SMCPP method, the core electrons are replaced by the norm-conserving pseudopotentials (PP) of Bachelet, Hamann and Schlüter (BHS),¹⁵ thus reducing the size of basis sets in two ways: (i) only the valence electrons are described in a many-body framework (Hartree–Fock approximation in the present implementation).^{3,16} As a consequence, the computational effort required to study scattering by targets with equal numbers of valence electrons is in general the same, regardless of how many core electrons are found in each molecule; (ii) these PP are soft and produce smooth, nodeless valence atomic wave functions. The use of BHS pseudopotentials also brings the advantage of incorporating relativistic corrections,¹⁵ which are important for heavier atoms.

In this work, we apply the same approach to study rotational excitation of XH_3 (X: N, P, As, Sb) by electron impact within the energy range from 7.5 up to 30 eV. The fixed-nuclei scattering amplitudes were calculated as described in Ref. 3, at the static-exchange (SE) approximation. All targets belong to the C_{3v} point-symmetry group and have permanent dipole moments. As a result, fixed-nuclei cross sections present a well-known divergent behavior in the forward direction. In this work, we will be concerned exclusively with rotational excitations from the rotational ground state of the targets, and this divergence will only be found in the dipole-allowed $00 \rightarrow 10$ rotational transition. Although the SMCPP procedure is useful to overcome the above referred computational limitations, it is impossible to couple an infinite number of partial waves numerically. As a result, SMCPP will not provide the expected divergent behavior, neither in the rotationally unresolved elastic DCS nor in the $00 \rightarrow 10$ rotational excitation DCS. However, in the case of elastic DCS, the SMCPP method gives reliable results (except near the forward direction) when the dipole moment of the target is small.¹⁷ In the present work, we have made use of the following scheme to deal with the long-range character of the dipole moment interaction: the SMCPP was used to describe the low values of the partial wave expansion of the scattering amplitude; the intermediate values and the large values were treated through closure formulas,^{18–20} where the intermediate l values were treated through the first Born approximation (FBA) of the full interaction potential and the large values ($l \rightarrow \infty$) were calculated using a closed form of the FBA for the dipole moment potential. Details will be given in Sec. II B.

In this paper, our goals are:

- (1) To observe the influence of the size of the central atom

in the scattering process. All molecules are of XH_3 type, where X atoms are in the same column of the Periodic Table (N, P, As and Sb);

- (2) To estimate rotationally elastic, inelastic and momentum transfer cross sections, which are useful in modeling gaseous discharge environments;
- (3) To carry out an interesting test of the SMCPP approach, by rotationally resolving the cross sections. (Unfortunately, to our knowledge, there are no rotationally resolved differential cross sections for the molecules considered here, except for NH_3 , and comparison with other results could only be made through rotationally summed cross sections, for PH_3 ^{4,21} and AsH_3 .²¹ Even for the lighter system (NH_3), the DCS for the dipole-allowed $00 \rightarrow 10$ rotational transition has never been reported);
- (4) To introduce such rotational cross sections in the literature, since, as we mentioned, we found no available similar ones. We hope that it may encourage experimentalists to try to rotationally resolve the cross sections, at least for NH_3 .

II. THEORETICAL FORMULATION

A. Dipole-forbidden rotational excitation

We have used a procedure similar to that of Refs. 13 and 22. A more detailed description is given by Brescansin *et al.*²² The elastic scattering amplitudes are calculated in the body-fixed frame (BF) of the molecular target applying the SMCPP method, and are then transformed into the laboratory-fixed frame (LF) through the relation

$$f^{\text{lab}}(\hat{k}'_{\text{out}}, \Omega, k_{\text{out}}, k_{\text{in}}) = \sum_{\ell\mu} Y_{\ell\mu}(\hat{k}'_{\text{out}}) f_{\ell\mu}^{\text{lab}}(\alpha, \beta, \gamma), \quad (1)$$

where

$$f_{\ell\mu}^{\text{lab}}(\alpha, \beta, \gamma) = \sum_m D_{\mu m}^{\ell}(-\gamma, -\beta, -\alpha) f_{\ell m}^B(\beta, \alpha). \quad (2)$$

In the above expressions, f^{lab} denotes the elastic scattering amplitude in the LF, $D_{\mu m}^{\ell}$ are Wigner rotation matrices²³ and $f_{\ell m}^B$ are the coefficients of the expansion of the BF scattering amplitude in spherical harmonics. It is also to be noted that \hat{k}'_{out} is the scattering direction in the LF, while $\mathbf{k}_{\text{in}} = (k_{\text{in}}, \theta_{\text{in}}, \phi_{\text{in}})$ and $\mathbf{k}_{\text{out}} = (k_{\text{out}}, \theta_{\text{out}}, \phi_{\text{out}})$ are, respectively, the wave vectors of the incident and outgoing particle in the BF. $\Omega = (\alpha, \beta, \gamma)$ denotes the Euler angles of the frame transformation. The Oz axis in the LF is defined along the incident direction $\hat{k}_{\text{in}} = (\alpha, \beta)$ with the Euler angle γ being arbitrary. The cross sections, remembering that the targets are symmetric-top molecules having $(2J + 1)$ degeneracies, are given by

TABLE I. Bond lengths (R) and rotational constants (A and B) for XH_3 .

System	R (Å)	A (10^{-4} eV)	B (10^{-4} eV)
NH_3	0.880	12.3	7.80
PH_3	1.415	4.74	5.78
AsH_3	1.519	4.35	4.65
SbH_3	1.707	3.48	3.64

$$\begin{aligned} \frac{d\sigma}{d\Omega}(\theta'_{\text{out}}, JK \rightarrow J'K') \\ = \frac{1}{2\pi} \frac{k_{J'K'}}{k_{JK}} \frac{1}{(2J+1)} \\ \times \sum_{M'} \int d\phi'_{\text{out}} |f^{\text{lab}}(\hat{k}'_{\text{out}}, JK M \rightarrow J'K' M')|^2, \end{aligned} \quad (3)$$

where

$$\begin{aligned} f^{\text{lab}}(\hat{k}'_{\text{out}}, JK M \rightarrow J'K' M') \\ = \int \Psi_{J'K'M'}^*(\Omega) f^{\text{lab}}(\hat{k}'_{\text{out}}, \Omega, k_{\text{out}}, k_{\text{in}}) \Psi_{JKM}(\Omega) d\Omega. \end{aligned} \quad (4)$$

In the above expression, $f^{\text{lab}}(\hat{k}'_{\text{out}}, JK M \rightarrow J'K' M')$ is the scattering amplitude for the $JKM \rightarrow J'K' M'$ transition, and Ψ_{JKM} are rotational eigenfunctions of the targets

$$\Psi_{JKM}(\Omega) = \left(\frac{2J+1}{8\pi^2} \right)^{1/2} D_{KM}^{J*}(\Omega), \quad (5)$$

where K and M are the projections of J along the BF and the LF Oz -axes, respectively. The rotational energies are calculated as

$$E_{JK} = BJ(J+1) + (A-B)K^2, \quad (6)$$

where the values of the rotational constants A and B used are shown in Table I, along with the molecular bond lengths.

We will consider electron scattering by molecular targets in the rotational ground state ($J=K=M=0$). As a consequence, the only dipole-allowed excitation will be $00 \rightarrow 10$, due to the well-known dipole selection rules,

$$J' = J \pm 1; K' = K. \quad (7)$$

B. Dipole-allowed rotational excitation

The following procedure was outlined in Sec. I. In a first level of approximation, we will treat the target as a rotating dipole, which interacts with the incident electron through

$$V = \frac{\mathbf{D} \cdot \hat{\mathbf{r}}}{r^2}, \quad (8)$$

where \mathbf{D} is the dipole moment of the target. Considering the above interaction potential, the FBA expression for the fixed-nuclei elastic scattering amplitude is given by

$$f_{\text{FBA}}^{\text{DIP}}(k, \hat{k}_{\text{in}}, \hat{k}_{\text{out}}) = 2i \frac{\mathbf{D} \cdot (\mathbf{k}_{\text{in}} - \mathbf{k}_{\text{out}})}{|\mathbf{k}_{\text{in}} - \mathbf{k}_{\text{out}}|^2}. \quad (9)$$

The above expression is very poor for the general description of the collision process, but it has three valuable properties: (i) it has a closed form and therefore holds in all partial waves up to $l \rightarrow \infty$; (ii) it is easily computed directly in the LF [in the LF, one finds $\hat{k}_{\text{in}} \equiv \hat{\mathbf{z}}$ and $\hat{D} = (-\gamma, -\beta)$]; (iii) it gives fair results in the large partial-wave limit. In the FBA, the rotational scattering amplitude for the $JKM \rightarrow J'K'M'$ excitation is given, in the LF, by

$$\begin{aligned} f_{\text{DFBA}}^{\text{DIP}}(JKM \rightarrow J'K'M'; \hat{k}'_{\text{out}}) \\ = \int d\Omega \Psi_{J'K'M'}^*(\Omega) f_{\text{FBA}}^{\text{DIP}}(\beta, \gamma, \hat{k}'_{\text{out}}) \Psi_{JKM}(\Omega). \end{aligned} \quad (10)$$

The superscript DFBA in Eq. (10) is to remind one that this expression for the rotational-excitation scattering amplitude is obtained with the first Born approximation of the dipole-moment potential. In order to improve the quality of our rotational scattering amplitude, we have used closure formulas and substituted the lowest partial waves of the above expression, up to some $l=l_1$, by those obtained with the SMCPP alone [as given by Eqs. (1) and (4)]. The choice of l_1 will be discussed later. The rotational scattering amplitude, which is now obtained combining SMCPP and DFBA procedures, is given by

$$\begin{aligned} f^{\text{lab}}(JKM \rightarrow J'K'M'; \hat{k}'_{\text{out}}) \\ = f_{\text{DFBA}}^{\text{DIP}}(JKM \rightarrow J'K'M'; \hat{k}'_{\text{out}}) + \sum_{l=0}^{l_1} \sum_{\mu} [f_{l\mu}^{\text{SMCPP}}(k_{\text{in}}, k_{\text{out}}) \\ - f_{l\mu}^{\text{DFBA}}(k_{\text{in}}, k_{\text{out}})] Y_{l\mu}(\hat{k}'_{\text{out}}), \end{aligned} \quad (11)$$

where $f_{l\mu}^{\text{DFBA}}$ are coefficients of the expansion of Eq. (10) in spherical harmonics. One should remember that the SMCPP method, in which the scattering wave function is expanded in a L^2 basis set, has an intrinsic short-range character. Therefore, there may be a gap between the (lower) partial waves well described by this method and those well described by the dipole-FBA (DFBA) procedure. To avoid such a gap, we substitute intermediate DFBA partial waves ($l_1 < l \leq l_2$) by partial waves calculated through the full-interaction-potential-FBA (FFBA). The resulting rotational scattering amplitude, obtained with the combination of DFBA, FFBA and SMCPP approaches, is given by

$$\begin{aligned} f^{\text{lab}}(JKM \rightarrow J'K'M'; \hat{k}'_{\text{out}}) \\ = f_{\text{DFBA}}^{\text{DIP}}(JKM \rightarrow J'K'M'; \hat{k}'_{\text{out}}) + \sum_{l=0}^{l_1} \sum_{\mu} [f_{l\mu}^{\text{SMCPP}}(k_{\text{in}}, k_{\text{out}}) \\ - f_{l\mu}^{\text{DFBA}}(k_{\text{in}}, k_{\text{out}})] Y_{l\mu}(\hat{k}'_{\text{out}}) + \sum_{l=l_1+1}^{l_2} \sum_{\mu} [f_{l\mu}^{\text{FFBA}}(k_{\text{in}}, k_{\text{out}}) \\ - f_{l\mu}^{\text{DFBA}}(k_{\text{in}}, k_{\text{out}})] Y_{l\mu}(\hat{k}'_{\text{out}}), \end{aligned} \quad (12)$$

where $f_{l\mu}^{\text{FFBA}}$ are coefficients of the expansion of the FFBA scattering amplitude in spherical harmonics. In order to calculate the FFBA rotational scattering amplitude, one should replace Eq. (8) by the full interaction potential, and follow the steps given by Eqs. (9) and (10). Expression (12) may

TABLE II. Cartesian Gaussians basis set used in NH_3 calculations.

Atom	Type	Exponents	Coefficient
N	<i>s</i>	17.567 31	1.000 000
		3.423 618	1.000 000
		0.884 299	1.000 000
		0.259 044	1.000 000
		0.055 707	1.000 000
		0.020 279	1.000 000
		0.005 070	1.000 000
		0.001 267	1.000 000
		0.000 317	1.000 000
		8.075 593	1.000 000
	<i>p</i>	2.923 253	1.000 000
		1.252 269	1.000 000
		0.511 100	1.000 000
		0.205 332	1.000 000
		0.079 058	1.000 000
		0.019 765	1.000 000
		0.004 941	1.000 000
		1.593 655	1.000 000
		0.453 504	1.000 000
		0.154 060	1.000 000
H	<i>s</i>	0.059 893	1.000 000
		13.361 50	0.130 844
		2.013 300	0.921 539
		0.453 800	1.000 000
	<i>p</i>	0.123 300	1.000 000
		0.750 000	1.000 000

be substituted in Eq. (3) to evaluate the dipole-allowed ($00 \rightarrow 10$) rotational excitation cross section. The choice of l_2 will also be discussed later.

To obtain the FFBA scattering amplitude, we must compute matrix elements of the full-interaction potential between two plane waves. In our method, this potential includes e^- -valence and e^- -core interactions, and we therefore have to calculate matrix elements of the PP between two plane waves. We give details of this procedure in Appendix B.

III. COMPUTATIONAL PROCEDURES

The BF elastic scattering amplitudes for e^- - XH_3 (X:P, As, and Sb) collisions were calculated as described in Ref. 3 at the experimental geometries (see Table I). The Cartesian Gaussian functions used to describe the valence part of NH_3 and also to represent the scattering wave function are shown in Table II. In all calculations performed, with the exception of the $00 \rightarrow 10$ excitation, the partial-wave decompositions of the elastic scattering amplitudes were truncated at $\ell=9$, and integrations were carried out using Gauss-Legendre quadratures with 392 points (14 for $0 \leq \theta \leq \pi$ and 28 for $0 \leq \phi \leq 2\pi$).

We have adopted the following criteria to choose the values of l_1 and l_2 : (i) since the SMCPP is a sophisticated method, which has led to faithful rotationally resolved cross sections,^{13,14} we decided to keep all information provided by it. To define the value of l_1 , we studied the convergence of the integral cross section (ICS) of the dipole-allowed $00 \rightarrow 10$ rotational excitation as a function of the number of partial waves used to expand the scattering amplitude ($l_{\text{max}} = 0, 1, 2, 3, \dots$). We therefore established that l_1 corresponds

TABLE III. Values of l_1 (SMCPP) and l_2 (DFBA+FFBA) for the XH_3 family.

Energy (eV)	System	l_1	l_2
7.5	NH_3	4	3
	PH_3	4	4
	AsH_3	4	4
	SbH_3	4	5
	NH_3	5	4
10	PH_3	4	4
	AsH_3	4	4
	SbH_3	4	6
	NH_3	5	4
	PH_3	4	4
15	AsH_3	5	5
	SbH_3	5	6
	NH_3	5	4
	PH_3	5	5
	AsH_3	5	5
20	SbH_3	5	7
	NH_3	5	5
	PH_3	5	5
	AsH_3	5	6
	SbH_3	6	8
25	NH_3	5	5
	PH_3	5	5
	AsH_3	5	6
	SbH_3	6	8
	NH_3	5	5
30	PH_3	5	6
	AsH_3	6	6
	SbH_3	6	8

to the partial wave for which the convergence of the ICS of the dipole-allowed rotational excitation was achieved (with four significant figures); (ii) to define the value of l_2 , we started from the DFBA scattering amplitude and progressively substituted its lower partial waves by those obtained through the FFBA procedure. We then established that l_2 corresponds to the partial wave for which convergence of the ICS of the dipole-allowed rotational excitation was achieved (with four significant figures). In other words, l_2 tells us where DFBA and FFBA partial waves become equivalent. To avoid the divergence at $\theta'_{\text{out}} = 0$, integration of the differential cross section (DCS) for the $00 \rightarrow 10$ transition was carried using Eq. (6) to make $k_{\text{in}} \neq k_{\text{out}}$ in Eq. (9), whenever Born closure procedure was applied. The values of l_1 and l_2 obtained with the above criteria are listed in Table III, for all molecules of the XH_3 family. Except in the case of SbH_3 , for which l_2 is greater than l_1 for all energies, we almost always found $l_1 \geq l_2$. This means that when $l_1 \geq l_2$, we do not need to use the FFBA partial waves, because SMCPP range is long enough to reach the region where DFBA and FFBA are equivalent. The discrepant behavior of SbH_3 may be related to the poor estimate obtained for the molecular dipole moment, as shown in Table IV. Its calculated value is

TABLE IV. Experimental and calculated dipole moments (Debye) for the XH_3 family.

	Experimental (D)	Calculated (D)	$\Delta\%$
NH_3	1.47	1.637	10.2
PH_3	0.58	0.728	20.3
AsH_3	0.20	0.261	23.4
SbH_3	0.12	-0.332	63.8

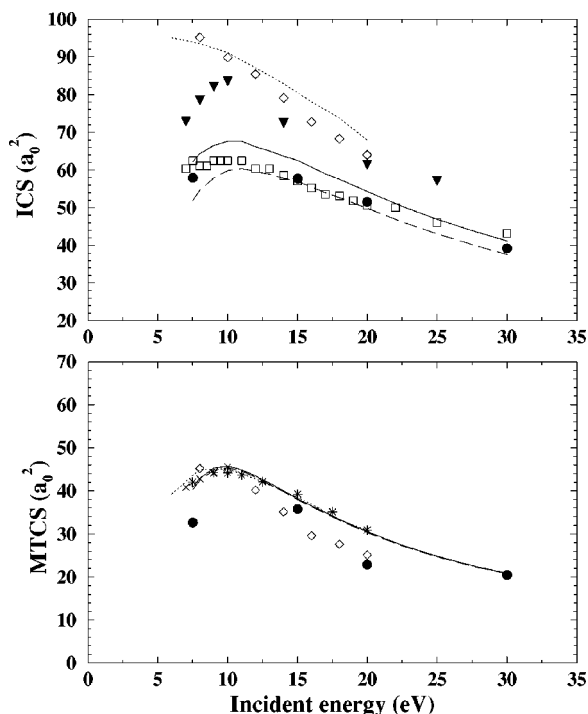


FIG. 1. Rotationally summed ICS and MTCS for NH_3 . Full line: present results (SMCPP+FBA); dashed line: present results (SMCPP only); dotted line: Yuan and Zhang (Ref. 24); crosses: Jain and Thompson (Ref. 8); stars: Pritchard *et al.* (Ref. 25); open diamonds: Gianturco (Ref. 9); bullets: Alle *et al.* (Ref. 26) (experimental); open squares: Sueoka *et al.* (Ref. 27) (experimental TCS); triangles: Szmykowski *et al.* (Ref. 28) (experimental TCS).

too high (even higher than the AsH_3 calculated dipole moment) and there was also inversion of the \vec{D} vector direction. We believe that this anomaly is due to the Hartree-Fock description of the target.

IV. RESULTS AND DISCUSSION

The elastic cross sections of PH_3 , AsH_3 and SbH_3 have been previously reported.³ Although this work is focused on rotational excitation cross sections, we will briefly compare our rotationally summed cross sections of NH_3 with other results, for completeness. In Fig. 1, we show rotationally summed integral and momentum transfer cross sections (ICS and MTCS) of NH_3 , in the energy range from 7.5 up to 30 eV. (We have included $00 \rightarrow 00$, $10, 20, 30, 3 \pm 3, 40, 4 \pm 3$ rotational excitations in the sum.) Present results are shown in two ways: (i) obtained with the SMCPP+DFBA procedure; and (ii) obtained with SMCPP only. We also show polarized elastic (rotationally unresolved) ICS and MTCS of Yuan and Zhang;²⁴ polarized rotationally summed ICS and MTCS of Gianturco;⁹ polarized MTCS of Jain and Thompson;⁸ static-exchange MTCS of Pritchard *et al.*;²⁵ and experimental data of Alle *et al.*²⁶ (elastic ICS and MTCS), of Sueoka *et al.*²⁷ (total cross section—TCS), and of Szmykowski *et al.*²⁸ (TCS). It is clear that all theoretical MTCS agree very well among themselves, being a little higher than the experimental results of Ref. 26. The calculations of Gianturco⁹ show some disagreement beyond 12 eV. Considering the ICS, on the other hand, one notices that our results are considerably lower than those of Refs. 9 and 24. Since the present results show a better agreement with the experimental data, their calculations may have overestimated the DCS for small scattering angles. It is interesting to observe, however, that the experimental data of Refs. 26–28 do not present good agreement among themselves.

We show rotationally summed DCS (RSDCS) in Figs. 2 (NH_3), 3 (PH_3), 4 (AsH_3) and 5 (SbH_3), at incident energies 7.5, 10, 15, 20, 25 and 30 eV. (Again, we have included $00 \rightarrow 00, 10, 20, 30, 3 \pm 3, 40, 4 \pm 3$ rotational excitations in the sum.) In each figure, we present our results in three dif-

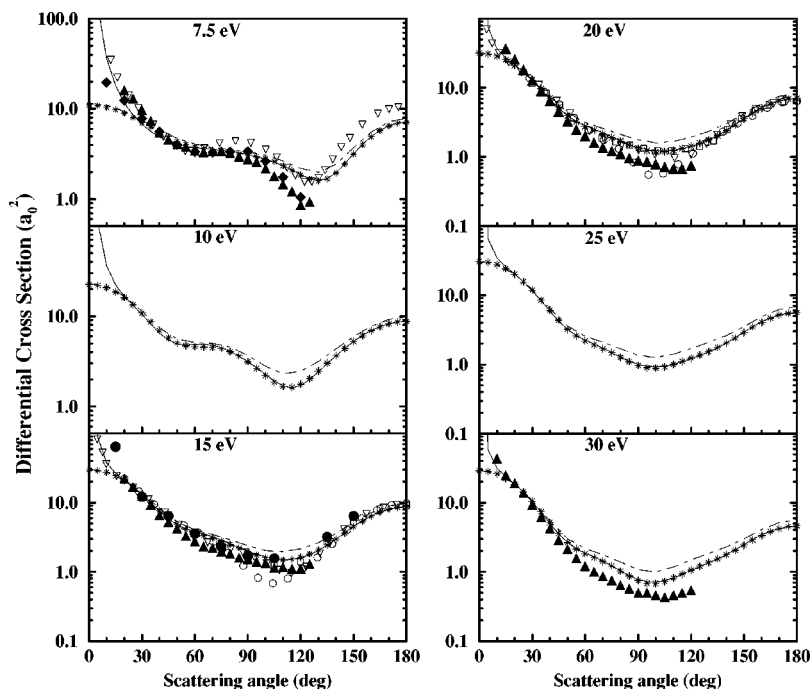


FIG. 2. Rotationally summed DCS of NH_3 . Full line: present results (SMCPP+FBA); crosses: present results (SMCPP); dot-dashed line: present results (elastic); open circles: Gianturco (Ref. 9) (15 and 20 eV); open squares: Pritchard *et al.* (Ref. 25) (15 and 20 eV); open triangles: Rescigno *et al.* (Ref. 18) (7.5, 15 and 20 eV); full circles: Shyn (Ref. 29) (experimental); full triangles: Alle *et al.* (Ref. 26) (experimental); full diamonds: Ben Arfa and Tronc (Ref. 30) (experimental).

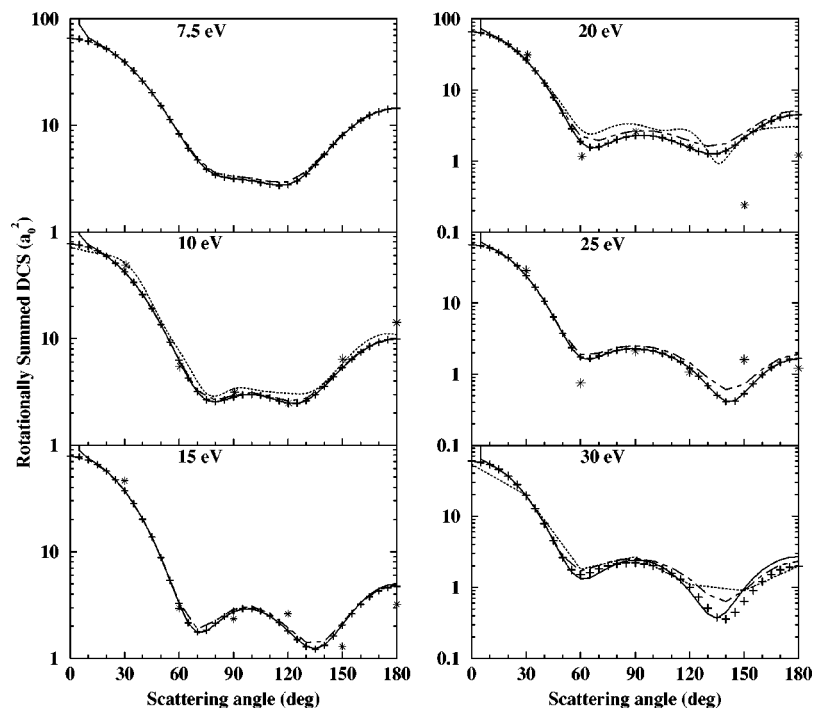


FIG. 3. Rotationally summed DCS of PH_3 . Full line: present results (SMCPP+FBA); crosses: present results (SMCPP); dot-dashed line: present results (elastic); dotted line: Winstead *et al.* (Ref. 31) (10, 20 and 30 eV); stars: Yaun and Zhang (Ref. 4) (10, 15, 20 and 25 eV).

ferent schemes: (a) RSDCS obtained with the SMCPP+DFBA+FFBA procedure (FFBA was applied only in the $l_2 > l_1$ cases. See Table IV; (b) RSDCS obtained with SMCPP only; and (c) rotationally unresolved (elastic) DCS obtained with SMCPP only. The agreement between the schemes (b) and (c) is very good. We observe that curves obtained in the scheme (b) are always close but below the curves obtained in the scheme (c), as expected. The fact that some discrepancy appears as we increase the incident energy and molecular size, and the fact that such discrepancy affects the angular region $\theta'_{\text{out}} > 90^\circ$ is well understood, and has

been discussed elsewhere.¹⁴ However, the agreement between the scheme (a) and the other two [(b) and (c)] depends on the molecule. For NH_3 , the dipole contribution becomes important for scattering angles below $\approx 25^\circ$; for PH_3 , below $\approx 10^\circ$; and for AsH_3 and SbH_3 , below $\approx 5^\circ$. This is certainly related to the dipole moment magnitude. For the heavier molecules (all but NH_3), we observe that cross sections obtained in the scheme (a) show an “elbow” near the forward scattering direction. This behavior will be discussed further. For the moment, it suffices to note that our results for NH_3 are in very good agreement with other calculations:

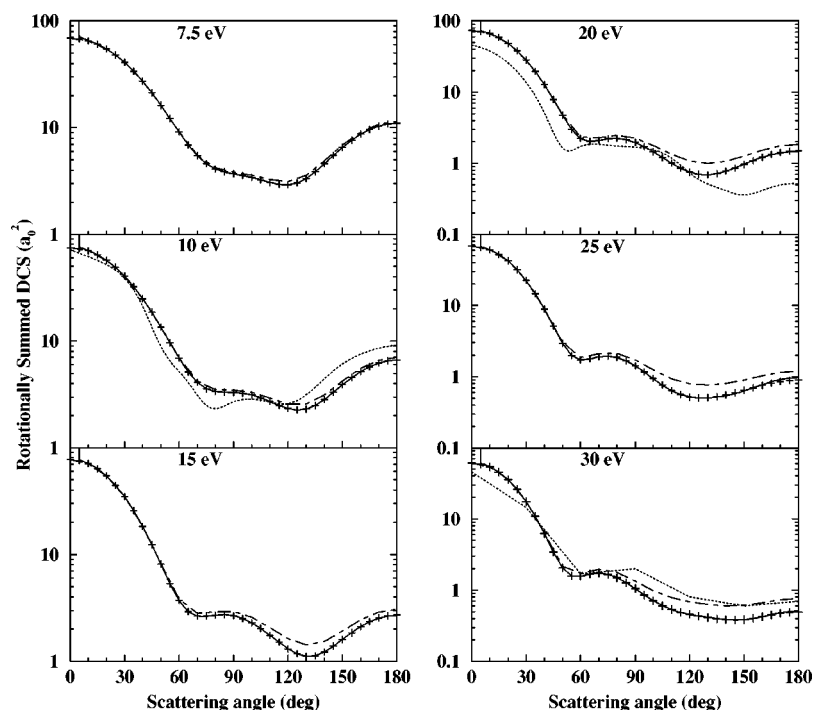


FIG. 4. Rotationally summed DCS of AsH_3 . Full line: present results (SMCPP+FBA); crosses: present results (SMCPP); dot-dashed line: present results (elastic); dotted line: Winstead *et al.* (Ref. 31) (10, 20 and 30 eV).

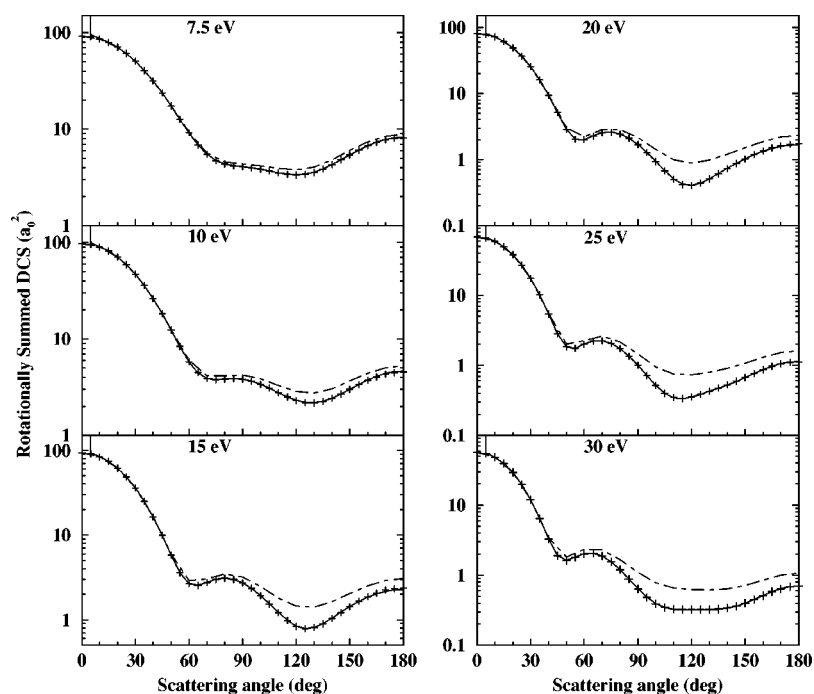


FIG. 5. Rotationally summed DCS of SbH_3 . Full line: present results (SMCPP+FBA); crosses: present results (SMCPP); dot-dashed line: present results (elastic).

RSDCS of Gianturco,⁹ and elastic DCS of Rescigno *et al.*¹⁸ and of Pritchard *et al.*²⁵ There is also good agreement with experimental data of Alle *et al.*,²⁶ Shyn²⁹ and of Ben Arfa and Tronc.³⁰ It is worth noting that the Born closure calculations are always closer to experimental points at small scattering angles. Our results also show good agreement with those of Yuan and Zhang⁴ and of Winstead *et al.*³¹ (elastic DCS) for PH_3 ; and of Winstead *et al.*³¹ (elastic DCS) for AsH_3 .

DCS for the dipole-allowed $00 \rightarrow 10$ transition are shown in Figs. 6 (NH_3), 7 (PH_3), 8 (AsH_3) and 9 (SbH_3), at 7.5, 10, 15, 20, 25 and 30 eV. Again, we present, for each mol-

ecule, results obtained in three different schemes: (d) with SMCPP ($0 \leq l \leq l_1$) + FFBA ($l_1 < l \leq l_2$) + DFBA ($l > l_2$) (FFBA was applied only in the $l_2 > l_1$ cases. See Table IV); (e) with SMCPP only; (f) with SMCPP ($0 \leq l \leq l_1$) + DFBA ($l > l_1$). Comparison between the schemes (d) and (f) reveals that the FFBA contribution to the cross sections is very modest, in all cases. In fact, the curves obtained in the schemes (d) and (f) are very close even for SbH_3 . If we recall all approximations made up to this point (fixed-nuclei, static-exchange, adiabatic-nuclei-rotation, Hartree-Fock, etc.) we will be able to conclude that the use of the FFBA procedure is not worthwhile, since its computational demand is signifi-

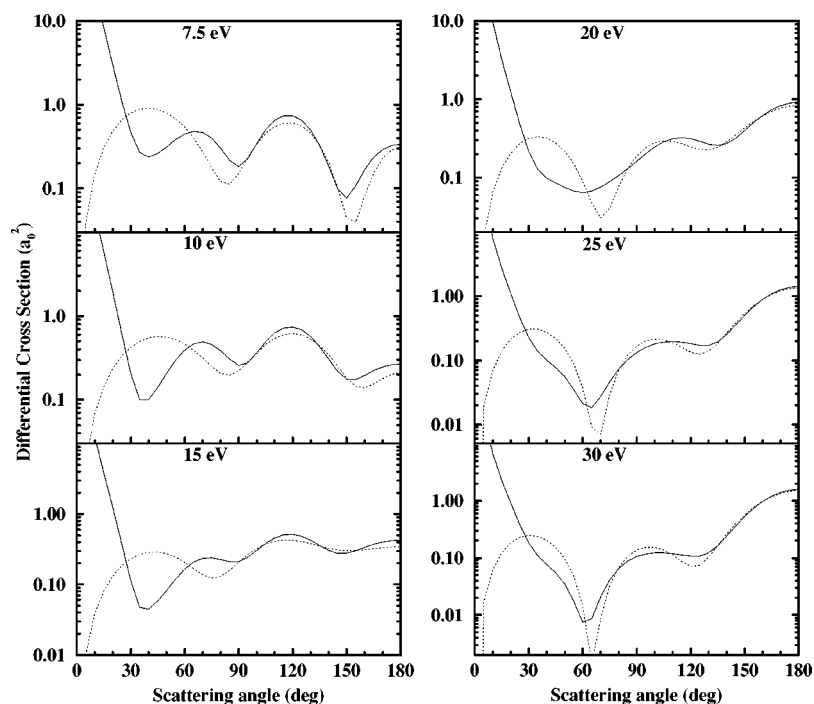


FIG. 6. DCS of NH_3 for the rotational excitation $00 \rightarrow 10$. Full line: SMCPP+DFBA; dotted line: SMCPP.

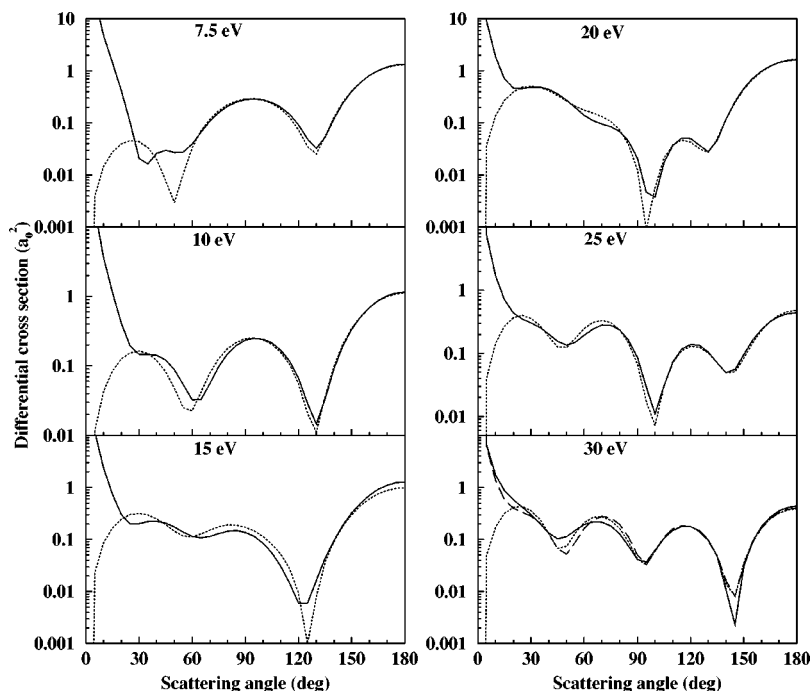


FIG. 7. DCS of PH_3 for the rotational excitation $00 \rightarrow 10$. Full line: SMCPP+FFBA+DFBA; long-dashed line: SMCPP+DFBA; dotted line: SMCPP.

cative. In other words, the SMCPP+DFBA procedure is sufficient. Comparing the results of the schemes (d)—or (f)—and (e), we find a behavior that had already been noticed in the RSDCS: the agreement is much better for the molecules with smaller dipole moments (AsH_3 and SbH_3) than for the more polar ones (NH_3 and PH_3). We believe this behavior was to be expected. For a given molecule, the discrepancies between (d)—or (f)—and (e) are generally larger at smaller energies, which may be due to the fact that long-range interactions are more relevant at such energies.

In Fig. 10 we show DCS for the rotationally elastic ($00 \rightarrow 00$) transition for the XH_3 family. The lighter molecule (NH_3) has a somewhat dissimilar behavior, which we

think is useful to understand the ‘‘elbow’’ that was observed in the RSDCS (Figs. 2 to 5) at $\theta'_{\text{out}} \approx 5^\circ$. The magnitude of the RSDCS (Figs. 2 to 5), near the forward scattering direction, is mainly determined by the contributions of the $00 \rightarrow 00$ transition (Fig. 10) and also by the dipole-allowed $00 \rightarrow 10$ transition (Figs. 6 to 9), *if the Born closure procedure is applied*. (It is to be observed that RSDCS obtained with SMCPP only, and rotationally elastic DCS, have almost the same value at $\theta'_{\text{out}} \approx 0^\circ$. Compare Fig. 10 with Figs. 2 to 5.) If a molecular target is highly polar, the contribution of the dipole-permitted $00 \rightarrow 10$ excitation will be significant not only in the vicinity of the origin ($\theta_{\text{out}} = 0$), and the RSDCS

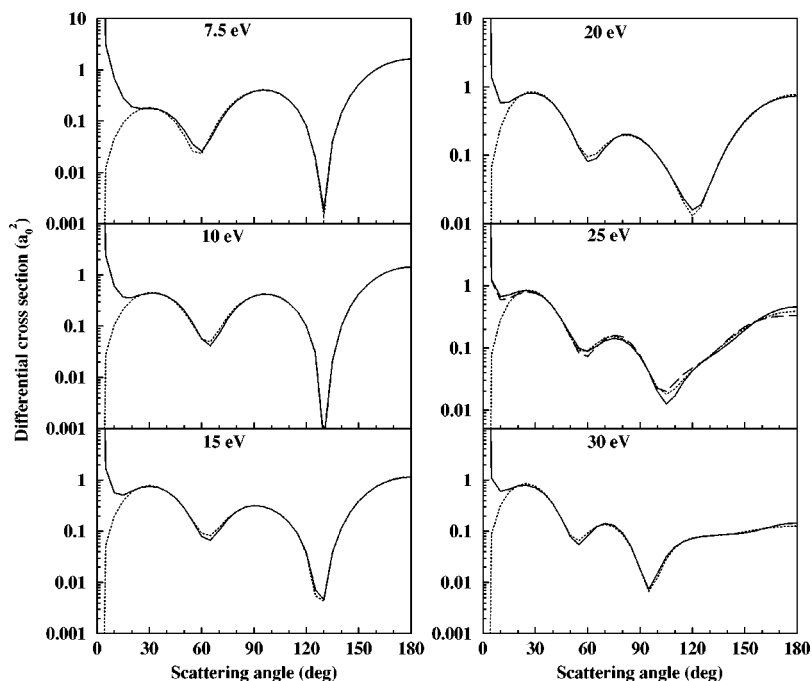


FIG. 8. DCS of AsH_3 for the rotational excitation $00 \rightarrow 10$. Full line: SMCPP+FFBA+DFBA; long-dashed line: SMCPP+DFBA; dotted line: SMCPP.

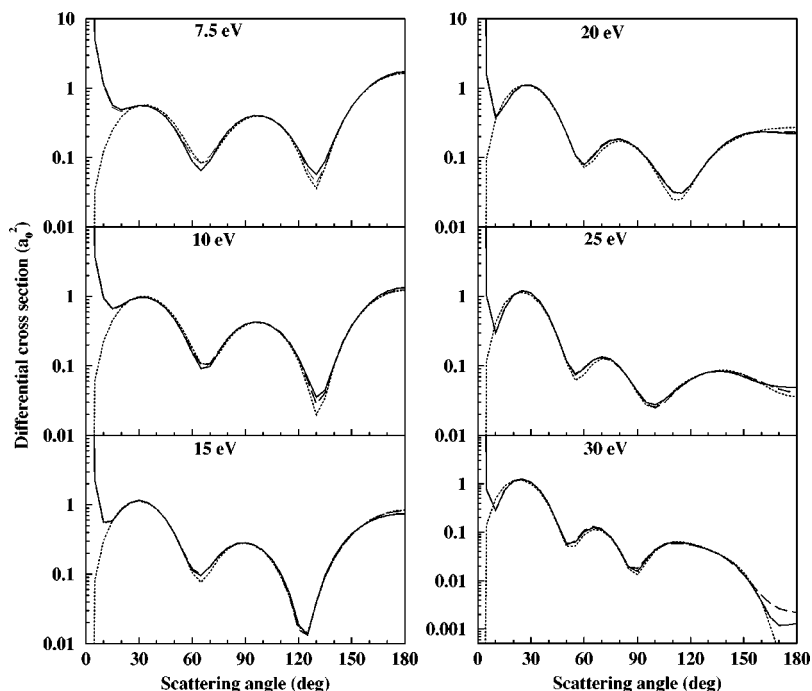


FIG. 9. DCS of SbH_3 for the rotational excitation $00 \rightarrow 10$. Full line: SMCPP+FFBA+DFBA; long-dashed line: SMCPP+DFBA; dotted line: SMCPP.

will be smooth. This is the case of NH_3 (Fig. 2). On the other hand, for weakly polar targets the $00 \rightarrow 10$ excitation contribution will be comparable in magnitude with the rotationally elastic one only near the origin, and the RSDCS will grow abruptly around $\theta_{\text{out}} \approx 5^\circ$. This is the case of SbH_3 (Fig. 5), where “elbows” are found in the RSDCS. It is clear that PH_3 and AsH_3 (Figs. 3 and 4) have intermediate behaviors between NH_3 and SbH_3 , as expected.

Although the RSDCS of AsH_3 (Fig. 4) and SbH_3 (Fig. 5) indicate that the FFBA partial waves do not significantly contribute to the cross sections, we performed extra calculations comparing (SMCPP+DFBA) and (FFBA+DFBA) schemes for the XH_3 molecules, in order to verify whether

the FFBA partial waves could lead to smoother RSDCS (without “elbows”). Though not shown here, it was verified that no significant contribution around $\theta_{\text{out}} \approx 5^\circ$ is provided by FFBA partial waves.

In order to understand what is going on, one should recall the approximations used: static-exchange (SE) and fixed-nuclei (FN). The divergent behavior of the elastic and dipole-allowed rotational DCS is a consequence of the FN approximation and, therefore, a formal unphysical result. In real life, nuclear positions may change, and no experimentalist will measure infinite cross sections. As a result, when we adopt the DFBA procedure, we are trying to improve our cross sections by including long-range interaction effects,

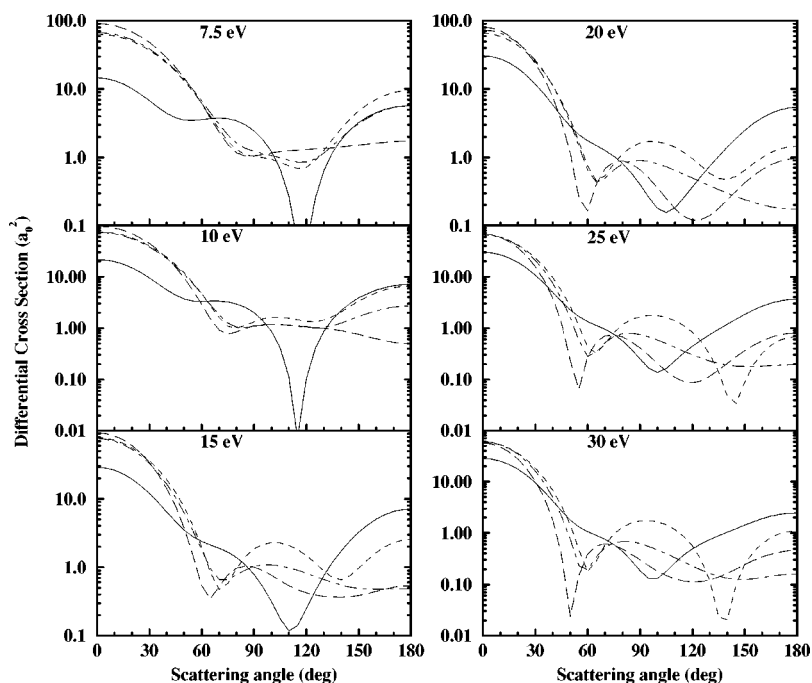


FIG. 10. DCS of XH_3 for the rotational excitation $00 \rightarrow 00$. Full line: NH_3 ; short-dashed line: PH_3 ; dot-dashed line: AsH_3 ; long-dashed line: SbH_3 .

but we must keep in mind that our calculations will be unphysical (divergent) at very small scattering angles ($\theta'_{\text{out}} \approx 0^\circ$). When one is dealing with highly polar targets, the DFBA contribution will provide significant contributions not only in the vicinity of $\theta_{\text{out}}=0$, and the quality of differential cross sections will be improved. For weakly polar targets, on the other hand, the DFBA procedure will significantly contribute only near the origin, where it diverges, and there will be no good reason to use it. (This work, along with unpublished results obtained for CH_3F and CH_3Cl , CClF_3 and CCl_3F , indicates that, within the energy range studied, the SMCPP+DFBA approach is worthwhile when the calculated dipole moments are higher than ~ 1 Debye.) In all cases, however, one should remember that the calculated results will be trustful only in the $5^\circ \leq \theta'_{\text{out}} \leq 180^\circ$ angular range. This does not constitute a severe limitation, since experimentalists also have problems near the incident beam direction, and are generally limited to scattering angles greater than 10 or 15° .

There is something else to be pointed out in the ‘‘elbow’’ discussion, and it is related to the SE approximation. It is known that the polarization potential has a long-range contribution, which asymptotically behaves as $\sim r^{-4}$, that could lead to smoother RSDCS (or elastic ones). Treating elastic $e^- - \text{C}_2\text{H}_2$ collisions, Mu-Tao *et al.*³² investigated this point, and found that such polarization effects significantly increased the cross sections around 5° .

In Fig. 11, we show rotationally elastic and rotationally summed inelastic ICS for the XH_3 family, including excitations $00 \rightarrow 10, 20, 30, 3 \pm 3, 4 \pm 3$. The ICS and momentum transfer cross sections (MTCS) for each excitation are shown in Tables V and VI, respectively. Both ICS and MTCS were calculated with Born closure. One may notice that although NH_3 has clearly smaller rotationally elastic ICS, all the XH_3

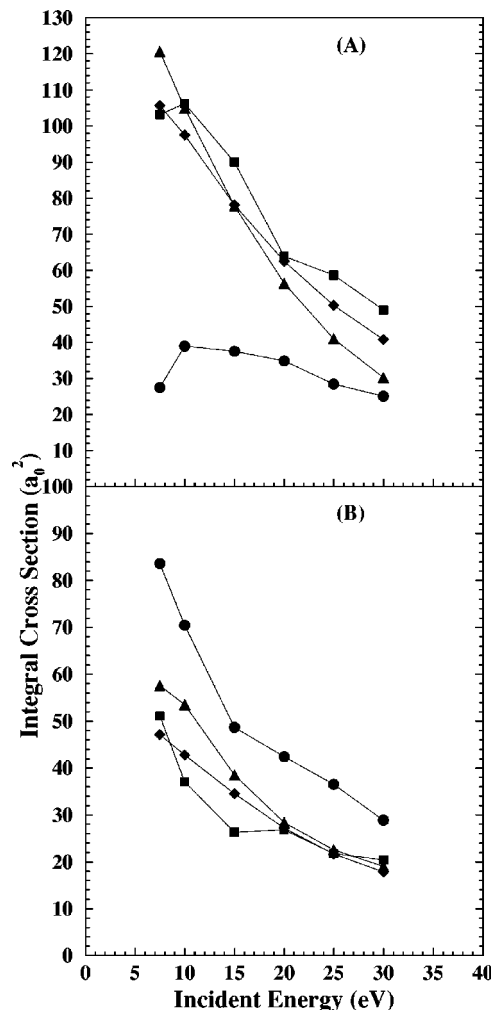


FIG. 11. ICS of XH_3 : (A) Rotationally elastic; (B) inelastic rotationally summed. Circles: NH_3 ; squares: PH_3 ; diamonds: AsH_3 ; triangles: SbH_3 .

TABLE V. Integral cross sections (a_0^2) for rotational excitations of XH_3 .

E (eV)	System	$00 \rightarrow 00$	$00 \rightarrow 10$	$00 \rightarrow 20$	$00 \rightarrow 30$	$00 \rightarrow 3 \pm 3$	$00 \rightarrow 40$	$00 \rightarrow 4 \pm 3$
7.5	NH_3	38.09	16.60	3.882	0.717	0.370	0.694	1.306
	PH_3	103.2	4.701	1.194	1.338	1.981	2.897	9.701
	AsH_3	105.7	3.320	0.845	2.107	1.706	3.852	8.986
	SbH_3	120.7	4.296	0.755	3.402	2.800	4.318	8.943
10	NH_3	43.07	13.55	4.039	0.901	0.774	0.558	2.425
	PH_3	106.2	4.077	0.969	1.107	1.571	1.587	5.223
	AsH_3	97.55	3.655	0.685	2.434	2.021	2.439	5.989
	SbH_3	105.0	4.865	0.523	3.484	2.808	2.683	6.075
15	NH_3	41.10	9.508	2.973	1.167	1.485	0.517	2.431
	PH_3	89.99	3.740	0.614	1.509	1.577	0.531	1.805
	AsH_3	78.06	3.652	0.343	2.358	1.709	1.227	3.284
	SbH_3	77.84	4.106	0.183	2.472	1.672	1.717	3.624
20	NH_3	36.78	7.825	1.957	1.267	1.470	0.332	1.812
	PH_3	63.81	3.977	1.212	2.092	1.145	0.701	1.530
	AsH_3	62.48	3.065	0.177	1.766	1.150	1.020	2.204
	SbH_3	56.41	3.123	0.129	1.587	1.046	1.683	2.441
25	NH_3	32.22	6.871	1.582	1.313	1.230	0.139	1.345
	PH_3	58.66	3.586	0.286	1.319	0.976	0.499	1.508
	AsH_3	50.29	2.499	0.124	1.300	0.811	1.043	1.788
	SbH_3	40.99	2.543	0.118	1.105	0.713	1.471	2.154
30	NH_3	28.39	6.139	1.402	1.208	1.061	0.082	1.036
	PH_3	49.05	3.512	0.233	1.270	0.833	0.712	1.546
	AsH_3	40.78	2.078	0.095	1.034	0.613	1.021	1.616
	SbH_3	30.28	2.258	0.090	0.851	0.542	1.218	1.974

TABLE VI. Momentum transfer cross sections (a_0^2) for rotational excitations of XH_3 .

E (eV)	System	$00 \rightarrow 00$	$00 \rightarrow 10$	$00 \rightarrow 20$	$00 \rightarrow 30$	$00 \rightarrow 3 \pm 3$	$00 \rightarrow 40$	$00 \rightarrow 4 \pm 3$
7.5	NH_3	26.52	4.938	4.327	0.810	0.381	0.486	1.569
	PH_3	40.96	3.079	1.257	1.560	1.497	2.761	9.696
	AsH_3	36.97	3.831	0.851	2.266	2.056	3.663	9.021
	SbH_3	33.82	4.198	0.628	3.767	2.902	4.233	9.379
10	NH_3	27.94	5.316	4.644	0.755	0.789	0.374	2.649
	PH_3	37.94	2.576	0.645	1.099	1.717	1.262	5.163
	AsH_3	28.87	3.665	0.496	2.076	1.961	2.294	5.972
	SbH_3	24.33	3.853	0.623	3.285	2.537	2.650	5.917
15	NH_3	21.88	4.139	2.840	1.085	1.505	0.462	2.375
	PH_3	26.83	2.109	0.347	1.154	1.418	0.412	1.832
	AsH_3	18.08	3.042	0.130	1.824	1.420	1.080	2.910
	SbH_3	14.38	2.825	0.082	1.925	1.364	1.564	2.757
20	NH_3	17.22	3.574	1.785	1.145	1.528	0.322	1.672
	PH_3	18.27	2.534	1.292	2.358	0.896	0.770	1.599
	AsH_3	12.40	2.161	0.065	1.325	0.875	0.872	1.812
	SbH_3	9.356	1.709	0.086	1.147	0.755	1.373	1.911
25	NH_3	13.73	3.345	1.352	1.222	1.266	0.143	1.173
	PH_3	15.03	1.646	0.206	0.831	0.677	0.458	1.436
	AsH_3	9.056	1.517	0.067	0.829	0.540	0.851	1.398
	SbH_3	6.558	1.011	0.114	0.698	0.436	1.109	1.560
30	NH_3	11.43	3.049	1.162	1.157	1.064	0.070	0.866
	PH_3	13.30	1.541	0.182	0.704	0.516	0.702	1.431
	AsH_3	6.999	1.030	0.068	0.559	0.349	0.802	1.191
	SbH_3	4.817	0.684	0.095	0.452	0.286	0.848	1.275

family presents comparable inelastic rotationally summed ICS. In the XH_3 family, the dipole-moment magnitude decreases as the molecular size increases, and these two competing features may be canceling each other, leading to somewhat similar rotationally inelastic cross sections.

In Fig. 12 and in Table VII we show, respectively, our rotationally resolved ICS ($00 \rightarrow 00, 10, 20$ excitations) and MTCS ($00 \rightarrow 00, 10, 20, 30$ excitations) for ammonia, comparing with those of Jain and Thompson⁸ (MTCS) and Gianturco⁹ (ICS and MTCS). The calculated rotationally elastic ICS of Gianturco are always higher than ours (about 20%), but are always lower than ours (about 25%) for the $00 \rightarrow 10$ rotational excitation. There is, however, a good agreement in shape. Our calculations are closer to those of Gianturco for the $00 \rightarrow 20$ ICS, but the curves cross each other. One finds similar agreement in the MTCS at 9 and 10 eV (Table VII). There is also a reasonable agreement between our MTCS and those of Jain and Thompson. Both calculations (Refs. 8 and 9) have included correlation-polarization model potentials, but we do not believe that any discrepancy is mainly due to this fact. It is well known that polarization effects do not play a relevant role at incident energies as high as the ones considered here.

V. CONCLUSIONS

The combination of the SMCPP method with the ANR approximation has provided a powerful procedure to calculate rotationally resolved cross sections for XH_3 molecules (X: N, P, As, Sb). The use of FFBA (one of the most time consuming steps in these calculations) to compute the intermediate partial waves was found to be dispensable in the estimate of the dipole-allowed $00 \rightarrow 10$ rotational excitation. Considering the covered energy range (7.5 up to 30 eV), the combination of the SMCPP and DFBA scattering amplitudes

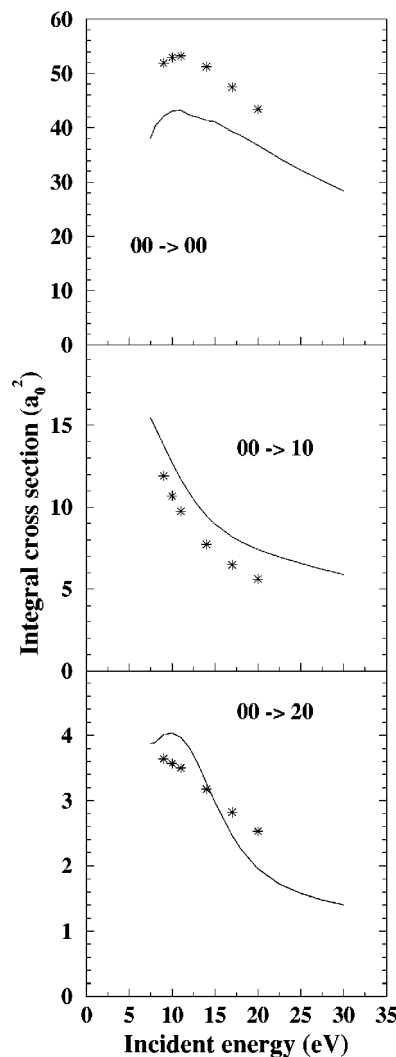


FIG. 12. Rotationally resolved ICS of NH_3 for $00 \rightarrow 00, 10, 20$ excitations. Solid line: present results; stars: Gianturco (Ref. 9).

TABLE VII. Momentum transfer cross sections (a_0^2) for rotational excitations of NH_3 .

Energy (eV)	Excitation	Present	Ref. 9	Ref. 8
8.0	00→00	27.89	...	28.76
	00→10	5.062	...	8.260
	00→20	4.398	...	6.228
	00→30	0.716	...	0.675
9.0	00→00	28.47	35.85	30.39
	00→10	5.275	4.892	7.928
	00→20	4.686	3.785	6.392
	00→30	0.701	...	0.782
10.0	00→00	27.94	35.10	30.97
	00→10	5.316	4.678	7.606
	00→20	4.644	3.642	6.356
	00→30	0.755	...	0.900

seems to be enough when the molecular dipole moment is greater than ~ 1 Debye. For weakly polar systems, however, the SMCPP method alone is able to provide reliable cross sections. Our RSDCS are in good agreement with other calculated elastic cross sections for NH_3 , PH_3 and AsH_3 , and also with available experimental data for NH_3 . The rotationally resolved ICS and MTCS obtained for ammonia show reasonable agreement with those of Gianturco⁹ (ICS and MTCS) and Jain and Thompson⁸ (MTCS).

ACKNOWLEDGMENTS

The authors acknowledge support from the Brazilian agency Conselho Nacional de Pesquisa e Desenvolvimento (CNPq). M.H.F.B. acknowledges partial support from Fundação da Universidade Federal do Paraná para o Desenvolvimento da Ciência, da Tecnologia e da Cultura (FUNPAR). Part of these calculations were performed at Centro Nacional de Processamento de Alto Desempenho em São Paulo (CENAPAD-SP). We would like to gratefully acknowledge Professor K. Jung for his solicitude and also for the helpful and enlightening material sent to us.

APPENDIX A: PROCEDURE FOR A MEASUREMENT OF ROTATIONALLY RESOLVED CROSS SECTIONS FOR NH_3

As was discussed previously, it is not feasible, at present, to have enough experimental resolution to distinguish each individual rotational line (energy separation $\sim 10^{-4}$ eV). However, we propose here a similar experiment as performed by Jung *et al.*⁶ The idea is that one might have enough resolution to measure a broadening in the rotational energy-loss peak. This can then be used, through a fitting procedure, to obtain information about the cross section for rotational excitations.

We start by writing the expression for the cross section for the transition $JK \rightarrow J'K'$,

$$a_{JK \rightarrow J'K'} = \sum_{J_i=|J'-J|}^{J'+J} [C(JJ_iJ'; KK_iK')]^2 a_{00 \rightarrow K_iJ_i}. \quad (\text{A1})$$

In the above expression, $C(JJ_iJ'; KK_iK')$ are Clebsch-Gordan coefficients and $a_{JK \rightarrow J'K'}$ are the rotational cross sections, apart from the kinematic factors k_f/k_i (since $k_f/k_i \approx 1$ within the energy range treated in this work, $a_{JK \rightarrow J'K'}$ may be understood as cross sections). If we now define the apparatus function⁶ as $f(E_0; \epsilon)$, where f (centered at E_0) is a function of the energy ϵ , we can write the intensity for the energy-loss peak, for a particular electronic and vibrational transition, as

$$I(\epsilon) = A \sum_{J,K} N^T(JK) \sum_{J',K'} a_{JK \rightarrow J'K'} f(\Delta E_{JK \rightarrow J'K'}; \epsilon), \quad (\text{A2})$$

where the constant A depends on the particular electronic and vibrational transition, as well as on quantities like density of the gas and electron current. $N^T(JK)$ is the rotational distribution for a given temperature T ,

$$N^T(JK) = \frac{(2J+1) \exp(-\beta E_{JK})}{Z}, \quad (\text{A3})$$

where $E_{JK} = BJ(J+1) + (A-B)K^2$, as in Eq. (6), $Z = \sum_{JK} (2J+1) \exp(-\beta E_{JK})$ is the partition function, and $\beta = 1/(k_B T)$, where k_B is the Boltzmann constant. (We have neglected nuclear spin effects.)

Equation (A2) above means that, at each possible energy loss value $\Delta E_{JK \rightarrow J'K'}$, where

$$\Delta E_{JK \rightarrow J'K'} = B\Delta J(2J+1 + \Delta J) + (A-B)\Delta K(2K + \Delta K), \quad (\text{A4})$$

with $J' = J + \Delta J$ and $K' = K + \Delta K$, we place an apparatus function $f(\Delta E_{JK \rightarrow J'K'}; \epsilon)$, and scale it by the probability that the initial state is populated [$N^T(JK)$] times the cross section for the transition. This expression for the intensity is the quantity that must be compared with the experimentally measured energy-loss curve.

If we now look at Eq. (A1), we see that all the cross sections for the $JK \rightarrow J'K'$ transitions can be written in terms of the cross section for the $00 \rightarrow J'K'$ transitions. From the results of our calculations, we conclude that only the $00 \rightarrow 00, 10, 20, 30, 3 \pm 3, 40, 4 \pm 3$ transitions are relevant. Therefore, for a given scattering angle, we have a total of seven fitting parameters to adjust the expression (A2) to the experimental results (remember that cross sections for $00 \rightarrow J \pm K$ transitions are equal). The idea is to rewrite Eq. (A2) in the following way:

$$I(\epsilon) = A \sum_{J'K'} I(\epsilon; 00 \rightarrow J'K') a_{00 \rightarrow J'K'}, \quad (\text{A5})$$

where the sum above is over the $00 \rightarrow 00, 10, 20, 30, 3 \pm 3, 40, 4 \pm 3$ transitions, and the $I(\epsilon; 00 \rightarrow J'K')$ are obtained from Eqs. (A1) and (A2). If now there is a set $\{\epsilon_i\}$ of energies where the rotational energy-loss curve has been measured, with intensities $I_i^{\text{exp}}(\epsilon_i)$, the cross sections $a_{00 \rightarrow J'K'}$ should be adjusted (fitting parameters) such that the quantity $\sum_i [I(\epsilon_i) - I_i^{\text{exp}}(\epsilon_i)]^2$, for example, is minimized.

A sketch of the procedure to extract the cross sections follows:

- (1) Choose temperature T ; calculate $N^T(JK)$ and use it to select the largest J to be used in Eq. (A2);
- (2) For each energy ϵ_i , calculate the $I(\epsilon_i; 00 \rightarrow J'K')$ [see Eq. (A5)];
- (3) Using some minimization procedure, obtain the cross sections $a_{00 \rightarrow J'K'}$ that minimize the sum $\sum_i (I(\epsilon_i) - I_i^{\text{exp}}(\epsilon_i))^2$.
- (4) If there are measurements of rotational energy-loss peaks for different scattering angles, the above procedure would result in differential cross sections for rotational excitations. One should note, however, that to obtain absolute cross sections, the constant A needs to be known.⁶

APPENDIX B: MATRIX ELEMENTS OF THE PSEUDOPOTENTIALS (PP) BETWEEN TWO PLANE WAVES

To obtain the FFBA scattering amplitude, we must compute the matrix elements of the pseudopotential operator given by

$$\hat{V}_{\text{PP}}(r) = \hat{V}_{\text{core}}(r) + \hat{V}_{\text{ion}}(r), \quad (\text{B1})$$

with

$$\hat{V}_{\text{core}}(r) = -\frac{Z_v}{r} \left[\sum_{i=1}^2 c_i^{\text{core}} \text{erf}[(\alpha_i^{\text{core}})^{1/2} r] \right], \quad (\text{B2})$$

and

$$\hat{V}_{\text{ion}}(r) = \sum_{n=0}^1 \sum_{j=1}^3 \sum_{l=0}^2 A_{njl} \sum_{m=-l}^{+l} |lm\rangle \langle lm|, \quad (\text{B3})$$

between two plane waves. These matrix elements were computed in a closed form³³ and are given by

$$\langle \mathbf{k}_f | \hat{V}_{\text{core}} | \mathbf{k}_i \rangle = -\frac{4\pi Z_v}{q^2} \sum_{i=1}^2 c_i^{\text{core}} \exp\left(-\frac{q^2}{4\alpha_i^{\text{core}}}\right), \quad (\text{B4})$$

where $q = |\mathbf{k}_i - \mathbf{k}_f|$, and

$$\begin{aligned} \langle \mathbf{k}_f | \hat{V}_{\text{ion}} | \mathbf{k}_i \rangle &= 4\pi \sum_{l=0}^2 (2l+1) P_l(\hat{\mathbf{k}}_i \cdot \hat{\mathbf{k}}_f) \\ &\times \sum_{n=0}^1 \sum_{j=1}^3 \frac{A_{njl}}{(\alpha_{jl})^{n+3/2}} T\left(2+2n, l, \frac{k_i}{\sqrt{\alpha_{jl}}}, \frac{k_f}{\sqrt{\alpha_{jl}}}\right), \end{aligned} \quad (\text{B5})$$

where

$$T(N, l, A, B) = \int_0^\infty dr r^N e^{-r^2} j_l(Ar) j_l(Br). \quad (\text{B6})$$

In the above expressions $P_l(u)$ are the Legendre polynomials, $j_l(x)$ are the spherical Bessel functions, Z_v is the valence charge of the atom, and in this application it is equal to 5 for all X atoms. The coefficients c_i^{core} , A_{njl} , and the decay constants α_i^{core} and α_{jl} are tabulated in Ref. 15.

- ¹K. Takayanagi and K. Itikawa, *Adv. At. Mol. Phys.* **6**, 105 (1970).
- ²A. Garscadden, *Z. Phys. D* **24**, 97 (1992). (All articles in this issue are devoted to relevant phenomena that take place in cold plasma.)
- ³M. H. F. Bettega, M. A. P. Lima, and L. G. Ferreira, *J. Chem. Phys.* **105**, 1029 (1996).
- ⁴J. Yuan and Z. Zhang, *Z. Phys. D* **28**, 207 (1993).
- ⁵D. W. Norcross and L. A. Collins, *Adv. At. Mol. Phys.* **18**, 341 (1982).
- ⁶K. Jung, Th. Antoni, R. Müller, K-H. Kochem, and H. Ehrhardt, *J. Phys. B* **15**, 3535 (1982).
- ⁷S. Altshuler, *Phys. Rev.* **107**, 114 (1957).
- ⁸A. Jain and D. G. Thompson, *J. Phys. B* **16**, 2593 (1983).
- ⁹F. A. Gianturco, *J. Phys. B* **24**, 4627 (1991).
- ¹⁰R. Müller, K. Jung, K-H. Kochem, W. Sohn, and H. Ehrhardt, *J. Phys. B* **18**, 3971 (1985).
- ¹¹F. H. Read, *J. Phys. B* **5**, 255 (1972).
- ¹²I. Shimamura, *J. Phys. B* **15**, 93 (1982).
- ¹³M. T. do N. Varella, M. H. F. Bettega, and M. A. P. Lima, *Z. Phys. D* **39**, 59 (1997).
- ¹⁴M. T. do N. Varella, A. P. P. Natalense, M. H. F. Bettega, and M. A. P. Lima, *Phys. Rev. A* (submitted).
- ¹⁵G. B. Bachelet, D. R. Hamann, and M. Schlüter, *Phys. Rev. B* **26**, 4199 (1982).
- ¹⁶M. H. F. Bettega, L. G. Ferreira, and M. A. P. Lima, *Phys. Rev. A* **47**, 1111 (1993).
- ¹⁷C. Winstead, Q. Sun, and V. McKoy, *J. Chem. Phys.* **96**, 4246 (1992).
- ¹⁸T. N. Rescigno, B. H. Lengsfeld, C. W. McCurdy, and S. D. Parker, *Phys. Rev. A* **45**, 7800 (1992).
- ¹⁹Q. Sun, C. Winstead, and V. McKoy, *Phys. Rev. A* **46**, 6987 (1992).
- ²⁰J. L. S. Lino, J. S. E. Germano, and M. A. P. Lima, *J. Phys. B* **27**, 1881 (1994).
- ²¹C. Winstead, Q. Sun, and V. McKoy, *J. Chem. Phys.* **96**, 4246 (1992).
- ²²L. M. Brescansin, M. A. P. Lima, and V. McKoy, *Phys. Rev. A* **40**, 5577 (1989).
- ²³M. E. Rose, *Elementary Theory of Angular Momentum* (Wiley, New York, 1957).
- ²⁴J. Yuan and Z. Zhang, *Phys. Rev. A* **45**, 4565 (1992).
- ²⁵H. P. Pritchard, M. A. P. Lima, and V. McKoy, *Phys. Rev. A* **39**, 2392 (1989).
- ²⁶D. T. Alle, R. J. Gulley, S. J. Buckman, and M. J. Brunger, *J. Phys. B* **25**, 1533 (1992).
- ²⁷O. Sueoka, S. Mori, and Y. Katayama, *J. Phys. B* **20**, 3237 (1987).
- ²⁸C. Szymkowski, K. Maciag, G. Karwasz, and D. Filipović, *J. Phys. B* **22**, 525 (1989).
- ²⁹T. W. Shyn (private communication).
- ³⁰M. Ben Arfa and M. Tronc, *J. Chim. Phys. Phys.-Chim. Biol.* **85**, 879 (1988).
- ³¹C. Winstead, Q. Sun, V. McKoy, J. L. da S. Lino, and M. A. P. Lima, *Z. Phys. D* **24**, 141 (1992).
- ³²L. Mu-Tao, L. M. Brescansin, M. A. P. Lima, L. E. Machado, and E. P. Leal, *J. Phys. B* **23**, 4331 (1990).
- ³³M. H. F. Bettega and L. G. Ferreira (unpublished).