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Cross sections for rotational excitation of CH_4 by 3–20-eV electrons

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We report calculated differential, integral, and momentum-transfer cross sections for rotational excitation of CH_4 by electron impact in the 3–20-eV energy range. These cross sections were derived from fixed-nuclei scattering amplitudes obtained using the Schwinger multichannel method. Our results represent the first rotational excitation cross sections obtained for a polyatomic molecule using entirely *ab initio* procedures. The cross sections agree well with those of earlier model-potential calculations. A comparison of these calculated cross sections with available experimental data is in general encouraging, but some discrepancies remain.

I. INTRODUCTION

Rotational excitation is an important energy-loss mechanism in collisions of low-energy electrons with molecules. Most *ab initio* studies of rotational excitation by electron impact have addressed linear molecules.[1] The situation, both theoretically and experimentally, is much less satisfactory for electron-polyatomic collisions. Rotational excitation cross sections have been obtained experimentally only for very few nonlinear polyatomic systems. In fact, the rotational excitation cross sections reported for e-H_2O collisions by Jung *et al.*[2] and for CH_4 by Müller *et al.*[3] and Tanaka[4] were obtained by a deconvolution of the vibrationally elastic peaks using an analysis due to Shimamura.[1] Direct measurement of rotational excitation cross sections for most molecules would require very high electron-energy resolution, not presently available.

On the theoretical side, there has also been limited progress. To date, most calculations of rotational excitation cross sections by electron impact have relied on model potentials. For example, in their studies of CH_4 Jain and Thompson[5] assumed a free-electron-gas model plus an orthogonalization procedure for the exchange interaction and a nonparametrized but approximate polarization potential. More recently, model exchange and polarization potentials have been used by Gianturco and coworkers[6–8] to calculate rotational excitation cross sections of CH_4 at several incident energies. Cross sections for the rotational transitions $0 \rightarrow 0$, $0 \rightarrow 3$, and $0 \rightarrow 4$ at 10 and 20 eV and the $0 \rightarrow 4$ at 0.5, 4, and 6 eV were studied.[6–8] Abusalbi *et al.*[9] have also obtained rotational excitation cross sections for CH_4 by 10-eV electrons using a local exchange and two different model polarization potentials. These studies[5,8,9] all make use of the adiabatic-nuclei-rotation (ANR) approximation.[1]

In this paper we report cross sections for rotational excitation of CH_4 by electrons from 3 to 20 eV using scattering amplitudes calculated as in Ref. 10 with the Schwinger multichannel method.[11,12] The Schwinger multichannel method is an L^2 approach to electron collisions in which the exchange interaction is properly treated and the polarization effects are taken into account via inclusion of energetically closed channels in a configuration-interaction-like expansion of the total scattering wave function. This approach has been used to study both linear[13–15] and nonlinear[16,17] systems in the past few years. An outline of the paper is as follows. In Sec. II we discuss the procedure used to obtain rotational excitation cross sections in the ANR approximation from the linear momentum body-frame scattering amplitude $f^B(\mathbf{k}_{\rm out},\mathbf{k}_{\rm in})$. In Sec. III we present our differential, integral, and momentum-transfer cross sections for the $0 \rightarrow 0$, $0 \rightarrow 3$, and $0 \rightarrow 4$ rotational excitation in CH_4 for impact energies from 3–20 eV and compare these results with those of other theoretical studies[5,8,9] and available experimental data. Section IV summarizes our results and conclusions.

II. METHOD

Our rotational excitation cross sections are obtained in the ANR approximation using body-frame full scattering amplitudes $f^B(\mathbf{k}_{\rm out},\mathbf{k}_{\rm in})$ calculated for e-CH_4 collisions with the Schwinger multichannel method.[10] The effects of exchange on the scattering amplitudes are properly included in these calculations while those of polarization are accounted for nonempirically[11,12,18] and should be adequately converged for the present applications.[10]

To obtain the laboratory-frame scattering amplitude, we first expand the dependence of the body-frame full scattering amplitude on $\mathbf{k}_{\rm out}$

TABLE I. Rotational excitation cross sections for CH_4.[a]

Impact		ICS[b]			MTCS[c]	
energy (eV)	0→0	0→3	0→4	0→0	0→3	0→4
3	32.64	0.025	0.279	22.21	0.025	0.310
5	46.60	0.888	1.807	37.59	0.905	1.754
7.5	62.93	2.305	6.025	50.97	2.537	5.866
10	68.48	3.731	10.60	46.56	3.812	10.06
15	52.32	5.117	6.150	32.13	4.500	5.434
20	38.31	7.148	6.245	19.47	6.412	5.405

[a] In atomic units.

[b] Integral cross sections.

[c] Momentum-transfer cross sections.

$$f^{B}(\mathbf{k}_{\text{out}},\mathbf{k}_{\text{in}})=\sum_{lm} Y_{lm}(\hat{\mathbf{k}}_{\text{out}})f^{B}_{lm}(k_{\text{out}},\hat{\mathbf{k}}_{\text{in}},k_{\text{in}}) \tag{1}$$

and then transform $Y_{lm}(\hat{\mathbf{k}}_{\text{out}})$ to the laboratory frame through the usual relation

$$Y_{lm}(\hat{\mathbf{k}}_{\text{out}})=\sum_{\mu} D^{l}_{\mu m}(-\gamma,-\beta,-\alpha)Y_{l\mu}(\hat{\mathbf{k}}'_{\text{out}}) \, , \tag{2}$$

where $\hat{\mathbf{k}}'_{\text{out}}$ is the scattering direction in the laboratory frame. In these equations the z axis is defined along the direction of incidence $\hat{\mathbf{k}}_{\text{in}}=(\beta,\alpha)$ with the remaining Euler angle γ arbitrary so far. Combining Eqs. (1) and (2) we can write

$$f^{\text{lab}}(\hat{\mathbf{k}}'_{\text{out}},\Omega,k_{\text{out}},k_{\text{in}})=\sum_{l\mu} Y_{l\mu}(\hat{\mathbf{k}}'_{\text{out}})f^{\text{lab}}_{l\mu}(\alpha,\beta,\gamma) \, , \tag{3}$$

where

$$f^{\text{lab}}_{l\mu}(\alpha,\beta,\gamma)=\sum_{m} D^{l}_{\mu m}(-\gamma,-\beta,-\alpha)f^{B}_{lm}(\beta,\alpha) \, , \tag{4}$$

$\Omega=(\alpha,\beta,\gamma)$, and $D^{l}_{\mu m}$ are the rotation matrices.[19] The CH_4 molecule is taken to be a spherical top, with rotational eigenfunctions given by[19,20]

$$\Psi_{JKM}(\Omega)=\left[\frac{2J+1}{8\pi^2}\right]D^{J*}_{KM}(\Omega) \, , \tag{5}$$

where K and M are the projections of J along the body- and laboratory-frame z axes, respectively.

In the ANR approximation the laboratory-frame scattering amplitude for the transition $JKM \rightarrow J'K'M'$ can be written as

TABLE II. Differential cross sections for rotational excitation of CH_4.[a,b]

Scattering		3 eV			5 eV	
angle (deg)	0→0	0→3	0→4	0→0	0→3	0→4
0	3.452	6.2[−17]	0.0276	5.773	3.7[−16]	0.229
10	3.519	9.2[−4]	0.0267	5.623	0.0025	0.223
20	3.715	0.0035	0.0244	5.296	0.0095	0.205
30	4.010	0.0071	0.0211	5.068	0.0205	0.181
40	4.335	0.0117	0.0179	5.146	0.0366	0.156
50	4.577	0.0171	0.0154	5.494	0.0587	0.137
60	4.604	0.0228	0.0143	5.820	0.0846	0.123
70	4.314	0.0278	0.0148	5.740	0.107	0.120
80	3.687	0.0309	0.0169	5.008	0.118	0.125
90	2.807	0.0309	0.0202	3.680	0.111	0.138
100	1.844	0.0278	0.0241	2.116	0.0916	0.152
110	1.006	0.0225	0.0275	0.840	0.0673	0.162
120	0.468	0.0168	0.0296	0.323	0.0484	0.163
130	0.315	0.0122	0.0301	0.792	0.0411	0.154
140	0.518	0.0103	0.0293	2.148	0.0459	0.137
150	0.954	0.0111	0.0277	4.014	0.0588	0.119
160	1.477	0.0138	0.0263	5.872	0.0738	0.105
170	1.825	0.0165	0.0253	7.221	0.0854	0.096
180	1.966	0.0176	0.0250	7.713	0.0897	0.093

[a] In atomic units.

[b] 9.2[−16] means 9.2×10^{-16}.

TABLE III. Differential cross sections for rotational excitation of CH_4.[a,b]

Scattering angle (deg)	7.5 eV			10 eV		
	0→0	0→3	0→4	0→0	0→3	0→4
0	18.11	1.3[−15]	0.602	32.43	2.1[−15]	1.026
10	17.02	0.0089	0.598	30.34	0.0224	1.022
20	14.19	0.0332	0.588	24.81	0.0837	1.012
30	10.73	0.0686	0.570	17.73	0.170	0.993
40	7.794	0.112	0.544	11.18	0.264	0.967
50	6.033	0.160	0.514	6.536	0.351	0.934
60	5.360	0.207	0.484	4.051	0.415	0.897
70	5.149	0.242	0.458	3.076	0.439	0.862
80	4.672	0.250	0.440	2.631	0.410	0.833
90	3.543	0.229	0.334	1.992	0.334	0.814
100	1.931	0.186	0.440	1.031	0.235	0.803
110	0.490	0.142	0.453	0.196	0.152	0.796
120	0.461	0.118	0.467	0.193	0.119	0.787
130	1.193	0.132	0.476	1.563	0.159	0.774
140	3.991	0.186	0.481	4.360	0.272	0.761
150	7.883	0.270	0.485	8.072	0.434	0.754
160	11.87	0.361	0.491	11.79	0.605	0.754
170	14.83	0.432	0.497	14.52	0.735	0.758
180	15.92	0.458	0.500	15.53	0.783	0.759

[a] In atomic units.
[b] 1.3[−15] means 1.3×10^{-15}.

$$f^{\mathrm{lab}}(\hat{\mathbf{k}}'_{\mathrm{out}},JKM\rightarrow J'K'M')=\int \Psi^{*}_{J'K'M'}(\Omega)f^{\mathrm{lab}}(\hat{\mathbf{k}}'_{\mathrm{out}},\Omega,k_{\mathrm{out}},k_{\mathrm{in}})\Psi_{JKM}(\Omega)d\Omega \tag{6}$$

and hence the differential cross sections are given by

$$\frac{d\sigma}{d\Omega}(\theta'_{\mathrm{out}},JKM\rightarrow J'K'M')=\frac{1}{2\pi}\frac{k_{J'K'M'}}{k_{JKM}}\int d\phi'_{\mathrm{out}}|f^{\mathrm{lab}}(\hat{\mathbf{k}}'_{\mathrm{out}},JKM\rightarrow J'K'M')|^2 \ . \tag{7}$$

TABLE IV. Differential cross sections for rotational excitation of CH_4.[a,b]

Scattering angle (deg)	15 eV			20 eV		
	0→0	0→3	0→4	0→0	0→3	0→4
0	30.55	2.4[−15]	0.488	26.05	2.5[−15]	0.495
10	28.30	0.0044	0.491	24.10	0.0053	0.502
20	22.47	0.162	0.502	19.06	0.198	0.522
30	15.26	0.321	0.520	12.81	0.398	0.554
40	8.908	0.486	0.542	7.278	0.610	0.592
50	4.671	0.624	0.566	3.510	0.794	0.622
60	2.560	0.705	0.587	1.543	0.914	0.636
70	1.780	0.703	0.600	0.786	0.942	0.631
80	1.425	0.611	0.605	0.566	0.866	0.611
90	0.973	0.453	0.597	0.453	0.706	0.578
100	0.422	0.285	0.569	0.340	0.511	0.532
110	0.122	0.164	0.514	0.335	0.342	0.473
120	0.470	0.124	0.434	0.592	0.248	0.402
130	1.640	0.166	0.343	1.179	0.247	0.329
140	3.481	0.266	0.261	2.026	0.329	0.268
150	5.596	0.394	0.203	2.970	0.460	0.229
160	7.509	0.518	0.173	3.815	0.599	0.210
170	8.821	0.607	0.160	4.395	0.704	0.203
180	9.285	0.639	0.157	4.601	0.743	0.202

[a] In atomic units.
[b] 2.4[−16] means 2.4×10^{-16}.

For a spherical top, levels with the same J but different K and M are degenerate and hence the cross sections of physical interest are obtained by summing over K' and M' and averaging over K and M. In this way we get

$$\frac{d\sigma}{d\Omega}(\theta'_{\rm out}, J\rightarrow J') = \frac{1}{2\pi}\frac{k_{J'}}{k_J}\frac{1}{(2J+1)^2} \times \sum_{\substack{KM\\K'M'}} \frac{d\sigma}{d\Omega}(\theta'_{\rm out}, JKM\rightarrow J'K'M') \; , \qquad (8a)$$

where

$$\frac{k_{JKM}^2}{2} = \frac{k_J^2}{2} = BJ(J+1) \; . \qquad (8b)$$

For CH_4 we take the rotational constant B equal to 6.551×10^{-4} eV.[5]

III. PROCEDURES AND RESULTS

The body-frame scattering amplitudes were obtained for elastic e-CH_4 collisions at impact energies from 3–20 eV. The details of the method and calculations are discussed in Ref. 10. The C-H internuclear separation is taken to be 2.05 a.u. The total scattering wave functions in these studies include contributions from the ${}^2A_1$, ${}^2A_2$, ${}^2B_1$, and ${}^2B_2$ symmetries in the C_{2v} point group. About 350 Slater determinants of ${}^2A_1$ symmetry and 150 to 200

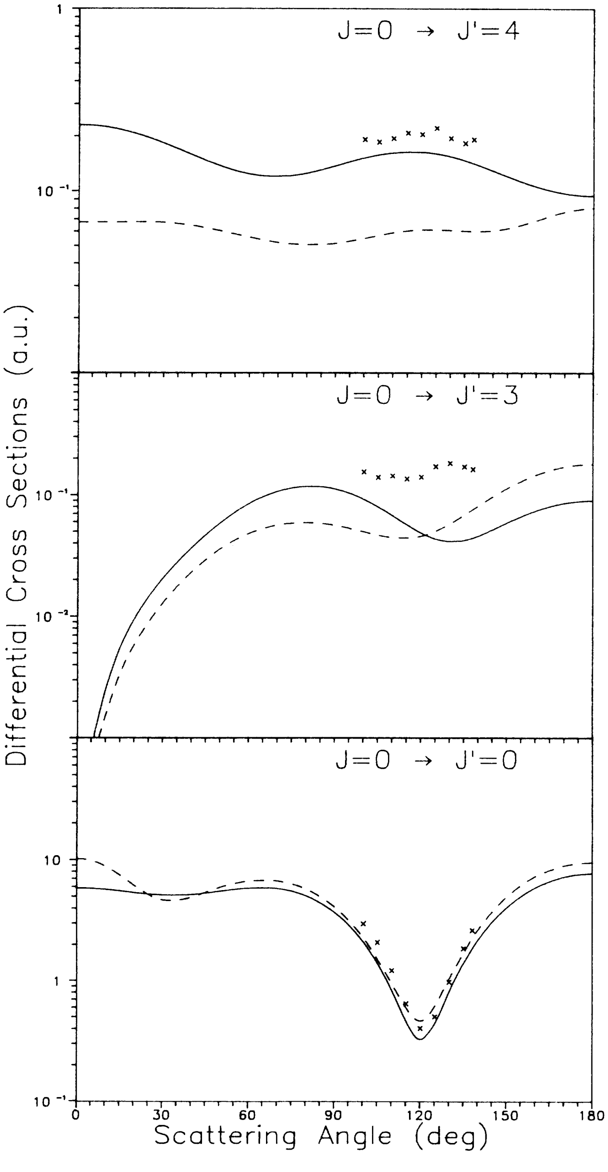

FIG. 1. Differential cross sections (DCS) for excitation of the $J=0\rightarrow J'=0,3,4$ transitions in CH_4 at 5 eV: ——, present results; — — —; calculated results of Ref. 5; × ×, experimental data of Ref. 3.

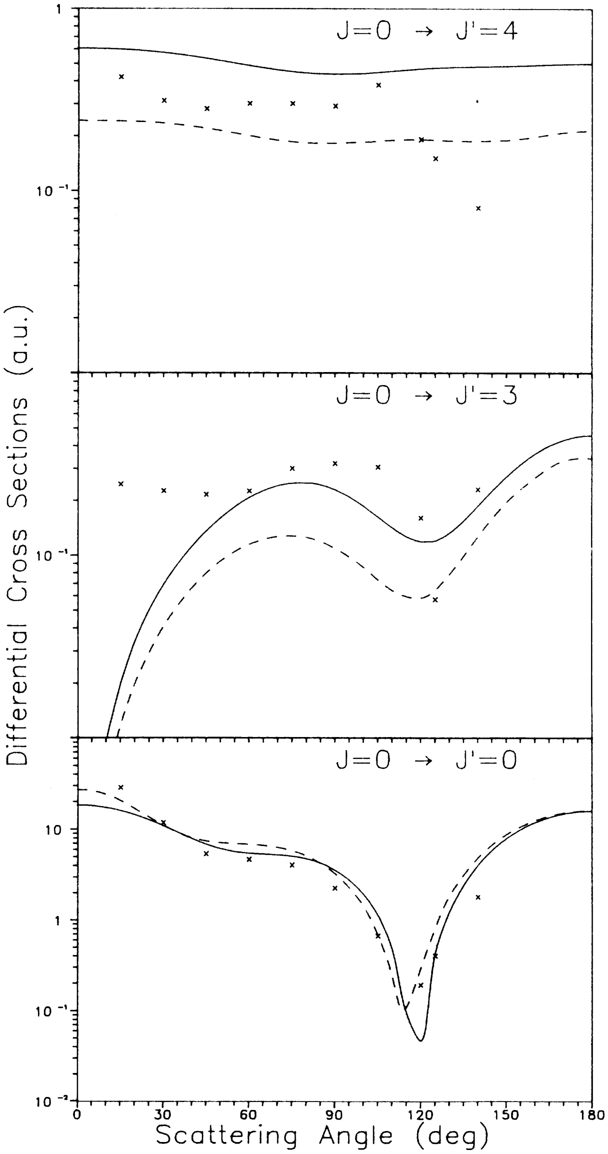

FIG. 2. Same as in Fig. 1 for 7.5 eV.

in each of the other symmetries were used in the expansion of the "closed-channel" part of the wave function to account for polarization effects.[10] The molecular orbitals in these Slater determinants were constructed from a basis of s, p, and d Cartesian Gaussian functions on the carbon and s functions on the hydrogens. The partial-wave decomposition in Eq. (1) was truncated at $l=5$. Explicit tests showed that higher partial waves lead to only negligible changes in the calculated differential cross sections (DCS). The angular integrations in Eqs. (6) and (7) were carried out using a Gauss-Legendre quadrature with 128 points (8 for $0 \le \theta \le \pi$ and 16 for $0 \le \phi \le 2\pi$).

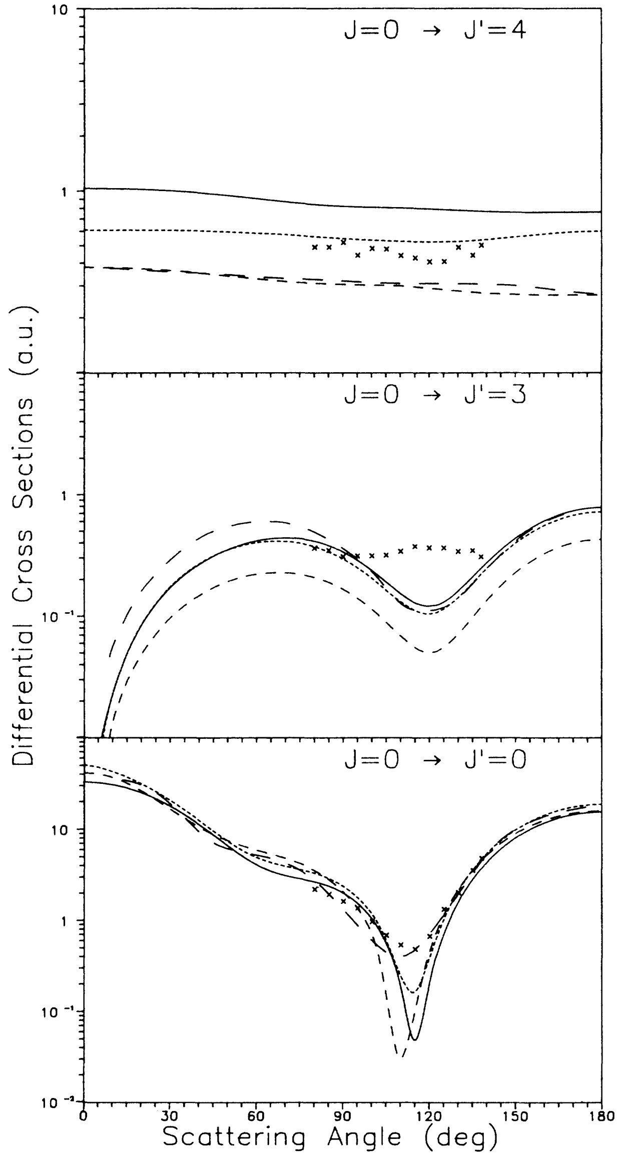

FIG. 3. DCS for rotational excitation of the $J=0 \rightarrow J'=0,3,4$ transitions in CH_4 at 10 eV: ——, present results; -----, calculated results of Ref 5; — — —, calculated results of Ref. 8; · · · ·, calculated results of Ref. 9; × ×, experimental data of Ref. 3.

The calculated integral cross sections (ICS) and momentum transfer (MTCS) rotational excitation cross sections for the 0→0, 0→3, and 0→4 transitions are given in Table I for impact energies of 3, 5, 7.5, 10, 15, and 20 eV. Tables II–IV list the corresponding differential cross sections. Figures 1, 2, and 3 show our DCS at 5, 7.5 and 10 eV, respectively, along with the available experimental data of Müller *et al.*,[3] and the theoretical results of Jain and Thompson.[5] For 10 eV, the calculated results of Gianturco[8] and Abusalbi *et al.*[9] are also included in Fig. 3 for comparison.

For incident energies of 5 and 7.5 eV, the agreement both in shape and magnitude between the theoretical results and experimental data is quite good. At 10 eV, all the calculated cross sections, except those of Ref. 8, exhibit a very deep minimum around 110°–120°, in strong contrast to the experimental data. For the 0→3 transition, the calculated cross sections fall abruptly to zero in the forward direction. The experimental data in this angular region, available only at 7.5 eV, do not show this feature. Beyond 60°, the agreement between our calculated and the measured DCS is, in general, good at 7.5 eV. This is in contrast to what is seen at 10 eV where all the calculated cross sections show a dip around 120°, while the experimental data are quite flat. At 5 eV the agreement between the calculated and experimental cross sections is poor between 90°–130°. For the 0→4 transition, as expected, the electron transfers almost all its angular momentum to the rotating target, resulting in very flat DCS for the energies studied here. Although the general agreement with the experimental data is reasonably good, our results do not show the sudden drop seen in the experimental DCS beyond 105° at 7.5 eV.

IV. CONCLUSIONS

Our calculated cross sections exhibit some discrepancies with the experimental data. In general, however, the agreement with results obtained using model potentials is good. For the 0→3 excitation the experimental cross sections do not exhibit a minimum around 120° at 10 eV nor do they show the pronounced decrease in the forward direction at 7.5 eV seen in the theoretical results. The calculated cross sections also do not account for the sudden fall beyond 105° for the 0→4 transition at 7.5 eV. Assuming, as in all theoretical studies to date, that the ANR approximation is suitable for methane treated as a spherical top, these discrepancies may suggest that the experimental findings, being indirect for the individual components, may not be on the sturdiest of grounds.

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