

Electron scattering from vibrationally excited CO₂ in the energy range of the ²Π_u shape resonance

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We measured the total electron scattering cross section for CO₂ in a time-of-flight gas-target transmission experiment at gas temperatures of 250 and 520 K in the energy range 0.5–9 eV. From measurements at both temperatures we determined the cross section for molecules in vibrationally excited states σ_{exc} and the ground-state cross section σ_0 . σ_{exc} exceeds σ_0 at all energies. A qualitative theoretical interpretation of this shift is possible on the basis of the calculated potentials from the CO₂⁻ compound state formed in the resonance scattering.

Stimulated by the work of Haddad and Elford,¹ who found evidence for a temperature dependence of the momentum-transfer cross section in an electron-swarm experiment with CO₂, Buckman, Elford, and Newman² performed a time-of-flight (TOF) gas-target transmission experiment which established that vibrationally excited CO₂, predominantly in the state (010), has a total electron scattering cross section which is much larger than that of the ground-state molecule at energies below 2 eV. Their exploratory measurements at the higher energies of 3.0, 3.8, and 14 eV revealed no significant differences of ground-state and excited-state cross sections. The larger cross section of the (010) state might be attributed to the electric dipole moment associated with bending vibrations.³

On the basis of our long experience with electron TOF spectrometers^{4–6} we have been developing a new spectrometer, specifically designed for studying electron-gas scattering at temperatures above and below room temperature.⁷ When we learned about the results of Buckman, Elford, and Newman—for which no other experimental or theoretical data exist for comparison—we decided to first employ our new spectrometer for the verification and extension of their work.

In the new spectrometer the gas target is part of the vacuum system; thus the wall of the target cell is accessible from the outside for efficient heating and cooling by means of a liquid thermostat (Fig. 1). With different liquids a wide temperature range can be covered. The temperature of 250 K was achieved with the liquid-nitrogen cooling of the methanol in the thermostat; the temperature of 520 K, by the electric heating of the silicone oil in the thermostat. The target temperature is determined with several calibrated sensors located on the outside wall of the target. At 520 K the temperature difference between the target outside and inside is 4 K.

Since the baratron manometer for determining the target-gas pressure is at room temperature, thermal-transpiration corrections^{8,9} are of utmost importance; in fact, these corrections are of the same order of magnitude as the cross-section changes with temperature. Test measurements with helium, for which no temperature dependence of the cross section exists, demonstrated that our

evaluation procedure is correct.

In our new spectrometer the electron bursts are produced by pulsing the Wehnelt electrode next to the cathode. During the “open time” of 6 ns the space-charge conditions in the cathode region change: The first electrons to pass the gate experience an additional acceleration due to the space-charge cloud behind them, but later, when the cloud electrons have all been extracted, the electrons are only accelerated by the potential between cathode and Wehnelt electrode.¹⁰ The resulting electron burst has an energy width of about 4 eV and, therefore, is very well suited for measurements presented here.

Shown in Fig. 2 are the cross sections measured with gas temperatures of 250 and 520 K; also shown are data points of Buckman, Elford, and Newman obtained at 573 K. The absolute uncertainty of the cross-section scale is estimated as $\pm 2.5\%$. The statistical error, which affects the curve values separately, is only about 1%. The agreement with Buckman, Elford, and Newman is excellent ex-

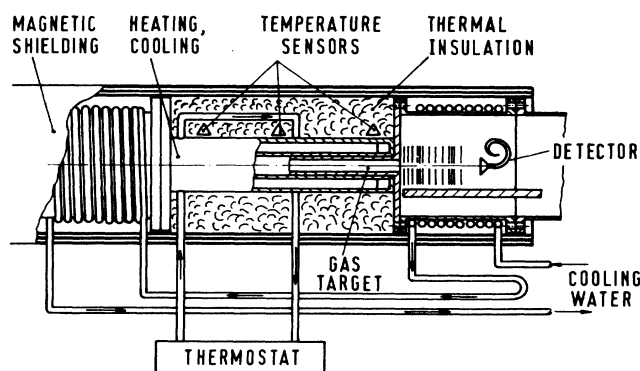


FIG. 1. Heating and cooling arrangement. The gas target is kept at a selected temperature by means of a liquid thermostat which is electrically insulated from the target. For maintaining target temperatures below room temperature the thermostat is cooled by liquid nitrogen. When the target is kept at high temperatures, the adjacent vacuum parts are cooled with water.

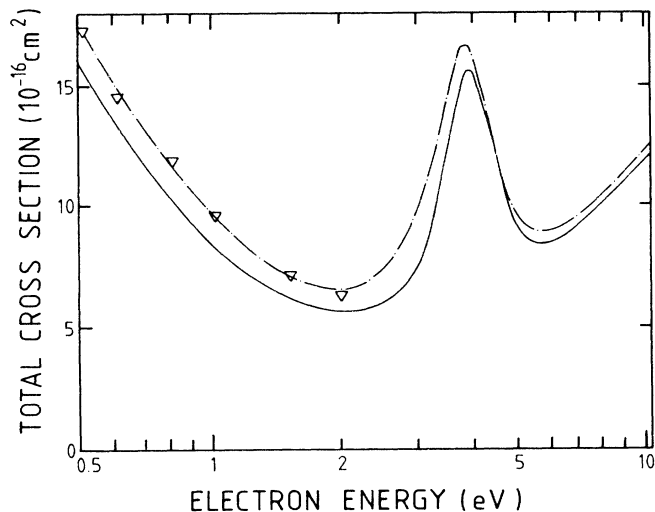


FIG. 2. Total cross sections for electron scattering from CO_2 at different gas temperatures. Solid line, 250 K; dashed line, 520 K; triangles, results of Buckman, Elford, and Newman for 573 K.

cept for their observation that $\sigma_{\text{exc}} \approx \sigma_0$ at 3.0 and 3.8 eV. In the peak region our 250-K measurements supersede our earlier 300-K measurements,¹¹ which were too low. The shape resonance has been well studied experimentally and theoretically,¹² but not with respect to total electron scattering from vibrationally excited molecules in bending modes.

Excitation energies and population fractions of the relevant vibrational states^{13,14} are given in Table I. In order to determine σ_{exc} and also σ_0 from the two measurements at 250 and 520 K we make the following approximations.

(i) The contribution from the asymmetric stretch mode (00^01) is negligible because of the very small population fraction.

(ii) The symmetric stretch mode (10^00), which has no electric dipole moment, has the same cross section as the ground state.

(iii) All the thermally populated bending modes have equal cross sections, here called σ_{exc} . Since there is as yet no theory about the influence of the bending vibration on the cross section, it is not obvious how a better approxi-

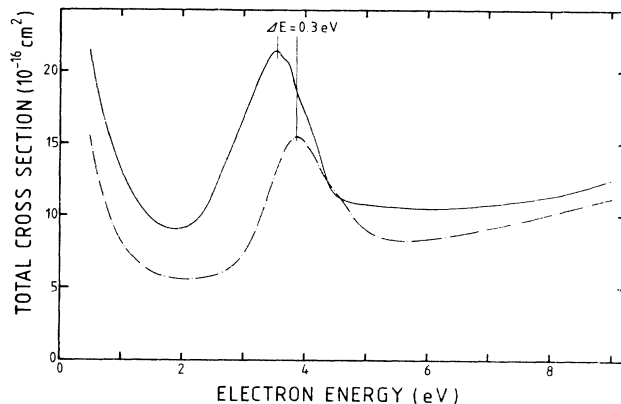


FIG. 3. Total cross sections for electron scattering from CO_2 molecules in the vibrational ground state σ_0 (dashed curve), and from molecules in excited states of bending vibration σ_{exc} (solid curve).

mation might be made.

The following equations result:

$$\sigma_0 = 1.172\sigma(250 \text{ K}) - 0.172\sigma(520 \text{ K}), \quad (1)$$

$$\sigma_{\text{exc}} = 3.856\sigma(520 \text{ K}) - 2.856\sigma(250 \text{ K}). \quad (2)$$

In order to estimate the errors made with these approximations we took the correct expressions for $\sigma(250 \text{ K})$ and $\sigma(520 \text{ K})$, corresponding to the population fractions of Table I, and inserted them into Eqs. (1) and (2) resulting in

$$\sigma_0 = \sigma((00^00)) \quad (3)$$

with about 99% purity, and

$$\begin{aligned} \sigma_{\text{exc}} = & 0.73\sigma((01^10)) + 0.13\sigma((02^20)) + 0.08\sigma((02^00)) \\ & + 0.02\sigma((03^10)) + 0.02\sigma((03^30)) + 0.02\sigma((11^10)) \\ & + 0.06[\sigma((10^00)) - \sigma((00^00))]. \end{aligned} \quad (4)$$

Thus our σ_0 describes $\sigma((00^00))$ in excellent approximation and σ_{exc} is predominantly determined by the cross section of the first bending mode (01^10) with a non-negligible admixture of (02^20) and (02^00). (See Table II.) Both cross-sections are plotted in Fig. 3.

TABLE I. Vibrationally excited states of CO_2 .

Threshold (meV)	State	Degeneracy	Population fraction	
			(at 250 K)	(at 520 K)
	(00^00)	1	0.9570	0.6942
82.75	(01^10)	2	0.0411	0.2191
159.37	(02^00)	1	0.0006	0.0198
165.54	(02^20)	2	0.0009	0.0345
172.11	(10^00)	1	0.0003	0.0149
239.59	(03^10)	2	0.0000	0.0066
248.38	(03^30)	2	0.0000	0.0054
257.50	(11^10)	2	0.0000	0.0044
291.26	(00^01)	1	0.0000	0.0010

The statistical error of about 1.5% for $\sigma(250\text{ K})$ and $\sigma(520\text{ K})$ leads to a statistical error of 1.7% for σ_0 and 4.5% for σ_{exc} . For the scale calibration of the cross-section axis we estimated a systematic error of 2.5%, as mentioned above. The energy resolution of the TOF method is energy dependent. At the energy of the resonance the resolvable energy is about 0.15 eV; therefore, the fine structure observed by Sanche and Schulz¹⁵ is not resolved here.

The comparison of σ_{exc} with σ_0 (Fig. 3) shows the following remarkable features.

(i) The nonresonant part of the cross section is larger over the whole energy range. The excess of σ_{exc} de-

TABLE II. Total electron scattering cross sections for CO_2 , σ_0 , and σ_{exc} , determined from measured cross sections according to Eqs. (1) and (2).

Energy (eV)	σ_0 (10^{-16} cm^2)	σ_{exc} (10^{-16} cm^2)
0.5	15.56	21.47
0.6	12.92	19.00
0.7	11.46	16.92
0.8	10.12	15.50
0.9	9.02	14.40
1.0	8.17	13.44
1.2	7.06	11.29
1.4	6.33	10.15
1.6	5.90	9.44
1.8	5.67	9.13
2.0	5.56	9.17
2.25	5.65	9.70
2.50	5.79	11.56
2.75	6.26	14.05
3.00	7.32	16.94
3.20	9.05	19.04
3.30	10.21	19.98
3.35	10.81	20.43
3.40	11.42	20.85
3.45	12.03	21.20
3.50	12.64	21.43
3.55	13.24	21.45
3.60	13.84	21.14
3.65	14.38	20.88
3.70	14.80	20.80
3.75	15.09	20.38
3.80	15.34	19.69
3.85	15.51	18.79
3.90	15.47	18.14
3.95	15.29	17.63
4.0	15.06	17.14
4.1	14.48	16.06
4.2	13.82	14.72
4.3	13.15	13.28
4.5	11.71	11.55
5.0	9.03	10.82
5.5	8.32	10.71
6.0	8.44	10.46
6.5	8.69	10.53
7.0	9.19	10.78
8.0	10.22	11.34
9.0	11.12	12.48

creases with energy from about 60% at 1 eV to 10% at 8 eV.

(ii) The $^2\Pi_u$ resonance peak is higher by about 35%, its full width at half maximum (FWHM) slightly wider (100 meV or about 8%), and—most noteworthy—the peak energy is shifted by 0.3 eV toward lower energy. This shift amounts to about $\frac{1}{4}$ of the resonance width. It is questionable whether the barely visible “fine structure” of the σ_{exc} resonance curve is genuine.

The observation (i) is an extension of the result of Buckman, Elford, and Newman² and qualitatively in accordance with the theoretical expectation for electron scattering from a molecule with an electric dipole moment produced by the bending vibration.³

The observation (ii) can be interpreted, at least qualitatively, by the symmetries of ground and excited states and the calculated potential curves for the CO_2^- compound state.¹⁶⁻¹⁸ The negative ion has its potential minimum at an O—C—O bending angle of $\theta=135^\circ$, far away from $\theta=180^\circ$ of the linear CO_2 molecule in its vibrational ground state. The transition from the linear molecule to a linear configuration of the negative ion (a “vertical” transition in the potential versus θ diagram) leads to a doubly degenerate Π_u state with $D_{\infty h}$ symmetry. A vertical transition from the (01^10) state of the molecule, which has an average bending angle of $\theta=175^\circ$ (that is, 5° of the linear configuration)¹⁹ and C_{2v} symmetry, removes this degeneracy. At this angle the negative ion can either be formed in the 2A_1 state, whose energy as function of the angle θ decreases rather rapidly toward the deep potential minimum at 135° , or in the 2B_1 state, whose potential curve has its minimum at $\theta=180^\circ$ but its slow increase as a function of θ is negligible between 180° and 175° . From the potential curves of those two states one would expect the following two overlapping resonance peaks: (i) one for the 2B_1 excitation at an energy which is lower than that of the resonance in the σ_0 cross section by 83 meV, the (01^10) excitation energy; (ii) and a second one for the 2A_1 excitation at a much lower energy. The energy shift of the second peak can be estimated by adding the 83 meV of the (01^10) excitation energy and about 270 meV for the difference of the 2A_1 potential energy at 175° and 180° . The energy shift of the unresolved doublet should lie in between, about $83+135\text{ meV}\approx 220\text{ meV}$ lower than the resonance in the σ_0 curve or even a little lower due to the admixture of molecules in higher modes of bending vibration. We conclude that the sign of the energy shift agrees with theoretical expectation and that the size of the shift is of the expected order of magnitude.

Our experimental result of a 300-meV energy shift and only a 100-meV increase in FWHM might indicate that the 2B_1 state is formed with a smaller probability than the 2A_1 state. Perhaps a detailed theoretical analysis of the Franck-Condon factors involved could provide elucidation. An additional complication, which ought to be considered in such an analysis, is the coupling of the 2A_1 and 2B_1 vibrational states by the Renner-Teller effect,²⁰ which could result in a single peak shifted to lower energy.

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