Elastic scattering of intermediate energy electrons by HCN[a)]

S. K. Srivastava, H. Tanaka,[b)] and A. Chutjian

Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California 91103
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Utilizing a crossed electron beam–molecular beam geometry and a relative gas flow technique, ratios $\sigma(\mathrm{HCN},\theta)/\sigma(\mathrm{He},\theta)$ of elastic differential cross sections of HCN to those of He have been measured at electron impact energies of 3,5,11.6, 21.6, and 50 eV and at scattering angles of 20° to 130°. Normalized absolute values of $\sigma(\mathrm{HCN},\theta)$ have been obtained by multiplying these ratios by the absolute values of $\sigma(\mathrm{He},\theta)$ reported previously. Since the rotational–vibrational structure in HCN was not resolved in the present measurements, the term elastic here includes contributions from elastic scattering, as well as from pure rotational and the 1-0, ν_2 vibrational excitations. The elastic differential cross sections have been compared with the predictions of the Born approximation and classical perturbation theory. For angular regions lying between 0° and 20°, and 130° and 180°, $\sigma(\mathrm{HCN},\theta)$ values have been obtained by extrapolation. These values have been used to calculate the integral and momentum-transfer cross sections.

I. INTRODUCTION

Recently, there has been a great deal of interest in the HCN molecule because of its applications in the CN laser system,[1] and its presence in comets and interstellar regions.[2] Also of note is the fact that its dipole moment (2.97 D) is larger than that critical value[3] (~1.625 D) at which polar molecules may support bound negative-ion states. This binding nature would be expected to affect the electron scattering behavior of HCN, and would, therefore, be of interest from the theoretical point of view.

Knowledge of low-to-intermediate energy (1–100 eV, say) electron scattering cross sections are needed in modeling the different laser, cometary, and interstellar plasmas. It is in this energy range that practically all elastic cross sections attain their maximum value. Moreover, theoretical calculations are most difficult to perform in this energy range (especially for polyatomic species), and experimental data are not available. These considerations prompted us to carry out a careful investigation of both elastic and inelastic[4] processes connected with the e–HCN interactions. In this paper we present normalized, absolute values of elastic differential, integral, and momentum-transfer cross sections. Due to insufficient electron energy resolution of the present experimental arrangement, the 1–0, ν_2 vibration of HCN could not be resolved. Therefore, the term elastic includes cross sections for elastic, pure rotational, and 1–0, ν_2 vibrational excitations.

II. APPARATUS AND METHOD

The experimental arrangement used in the present measurements has been described in detail previously.[5,6] Briefly, a crossed electron beam–molecular beam scattering geometry was employed. A well defined molecular beam was formed by flowing HCN through a capillary array. In order to keep HCN in the vapor phase, the gas handling system, consisting of stainless steel connecting tubes and leak valves, was heated to a temperature of about 50 °C.

The HCN beam is crossed at 90° by a beam of monoenergetic electrons of fixed impact energy. At a particular scattering angle θ, scattered elastic electrons are focused, energy analyzed, and detected. Conventional pulse detection and multichannel scaling methods are used to obtain the elastic scattering spectrum.

As in previous works, the electron energy analyzer was fixed, and the electron gun rotated about the scattering center to obtain the angular distribution of elastic-scattered electrons. At each angle θ, elastically scattered signals were recorded, and the integral counts were noted. The scattered, integrated intensity $\dot{N}_e(A,\theta)$ for a particular species A at an angle θ is directly proportional to the differential cross section (DCS) $\sigma(A,\theta)$ by the relation

$$\dot{N}_e(A,\ \theta)=K(A,\ \theta)\,\sigma(A,\ \theta). \tag{1}$$

In order to obtain the absolute value of $\sigma(A,\ \theta)$, one has to measure the absolute value of $K(A,\ \theta)$, which depends on several quantities[5] such as incident electron current, density of target species, geometrical overlap factors, efficiency of the detector system, etc. At low impact energies, it is not possible to measure accurate absolute values of these quantities. Therefore, a method was developed[5] which utilized the helium DCS as a secondary standard to obtain absolute values of $K(A,\ \theta)$ for the range of experimental θ at each impact energy. They were then used to determine absolute values of $\sigma(A,\ \theta)$. Details of this method are given in Ref. 5. To summarize, HCN was first flowed through the capillary array, and the scattered electron intensity $\dot{N}_e(\mathrm{HCN},\ \theta)$, the flow rate of HCN through the capillary array $\dot{N}(\mathrm{HCN})$, and pressure $p(\mathrm{HCN})$ behind the capillary array were measured. Then, the flow of HCN was replaced by He in such a way that all other experimental conditions such as incident electron current, sensitivity of the detector system, overlap geometry, etc., remained unchanged. The corresponding quantities $\dot{N}_e(\mathrm{He},\ \theta)$, $\dot{N}(\mathrm{He})$, and $p(\mathrm{He})$ were measured once again. The two DCS [$\sigma(\mathrm{HCN},\ \theta)$ and $\sigma(\mathrm{He},\ \theta)$] are related to these quantities through the following relations:

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b)NRC–NASA Resident Research Associate.

TABLE I. Elastic differential cross-section ratios $\sigma(\mathrm{HCN}, \theta)/\sigma(\mathrm{He}, \theta)$. Errors are estimated to be ± 10%.

θ (deg) \ E_0 (eV)	3	5	11.6	21.6	50
20	23	20	16	9.0	7.3
30	16	11	8.8	5.4	3.8
40	11	8.0	6.4	3.7	2.4
50	7.8	5.7	4.7	2.5	1.7
60	4.6	3.0	3.1	1.8	1.3
70	3.1	2.5	2.2	1.3	1.1
80	2.8	2.2	2.0	1.1	1.3
90	1.9	2.0	1.9	1.2	1.3
100	1.6	1.8	1.8	1.5	1.7
110	1.6	1.8	1.8	1.6	1.9
120	1.7	1.7	1.2	1.2	3.3
130	2.0	1.8	1.6	2.4	4.5

$$\sigma(\mathrm{HCN}, \theta)/\sigma(\mathrm{He}, \theta)$$
$$= [\dot{N}_e(\mathrm{HCN}, \theta)/\dot{N}_e(\mathrm{He}, \theta)]$$
$$[m(\mathrm{He})/m(\mathrm{HCN})]^{1/2}[\dot{N}(\mathrm{He})/\dot{N}(\mathrm{HCN})], \tag{2}$$
$$= [\dot{N}_e(\mathrm{HCN}), \theta)/\dot{N}_e(\mathrm{He}, \theta)][p(\mathrm{He})/p(\mathrm{HCN})], \tag{3}$$

where m(HCN) and m(He) are the molecular and atomic weights of HCN and He, respectively.

In order to obtain the values of $\sigma(\mathrm{HCN}, \theta)$, the absolute values of $\sigma(\mathrm{He}, \theta)$ are needed. For this purpose, we chose the experimental results of Andrick and Bitsch[7] and McConkey and Preston.[8] The reasons for choosing their values will be discussed in detail in the next section.

As a routine, we followed certain precautions for minimizing the errors in our measurements. They are as follows:

(i) The incident electron-beam energy was calibrated by observing the 19.35 eV resonance in helium at $\theta = 90°$.

(ii) The true zero angle was measured by observing the nominal angle about which $2\,^1P$ excitation in helium was symmetric.

(iii) At small angles there was a possibility that the direct beam would be detected: hence, the measurement of the elastic-scattered intensity would be in error To check this, the main gas beam was turned off and a side leak to the scattering chamber was opened to establish the same background pressure in the scattering chamber as when the beam was on. The direct electron beam was then monitored as a function of angle. It was found that at low electron impact energies ($E_0 \leq 20$ eV), the direct beam contribution was insignificant ($\leq 1\%$) for scattering angles of 20° or larger.

(iv) The pressure p(He) or P(HCN) [see Eq. (3)] behind the capillary array was determined by a factory-calibrated Wallace and Tiernan gage. In order to check the accuracy of the pressure measurements, we also measured the flow rates of the gases and used both Eqs. (2) and (3) to obtain the cross section ratios. These ratios agreed within 5% to one another. Further details concerning this may be found in Ref. 5.

In addition, due to the toxic nature of HCN, certain safety precautions had to be taken. These precautions were the same as those summarized in Ref. 4.

III. RESULTS AND DISCUSSION

Measured ratios $\sigma(\mathrm{HCN}, \theta)/\sigma(\mathrm{He}, \theta)$ at electron impact energies of 3, 5, 11.6, 21.6, and 50 eV are presented in Table I. The estimated error for these ratios is about ± 10%. This value has been obtained by considering all possible sources of errors in the measurements. These errors are explained in detail in Table II of Ref. 5.

In order to obtain the absolute values of $\sigma(\mathrm{HCN}, \theta)$, the absolute values of $\sigma(\mathrm{He}, \theta)$ are needed. For the electron impact energy region of 1 to 100 eV, several[7–11] experimental results on the elastic scattering cross sections of helium are available. A survey of recent measurements is presented in Ref. 10. In the present work, at electron impact energies of 3, 5, and 11.6 eV, the results of Andrick and Bitsch[7] were used. They are the only results which provide $\sigma(\mathrm{He}, \theta)$ values for the entire angular range covered by the present experiment—20° to 130°. Values of $\sigma(\mathrm{He}, \theta)$ at 11.6 eV were obtained by interpolating their results at 10 and 12 eV. For the electron impact energy of 21.6 eV, the $\sigma(\mathrm{He}, \theta)$ values were determined by interpolating the results of McConkey and Preston[8] who have measured elastic scattering cross sections of helium in the energy region of 1 to 100 eV and angular range of 20° to 90°. Since there are no resonances in the vicinity of 11.6 and 21.6 eV, it is felt that these interpolations are quite accurate. At 50 eV electron impact energy, there are two experimental measurements—one by McConkey and Preston[8] and the other by Crooks and Rudd.[9] For the sake of uniformity we chose $\sigma(\mathrm{He}, \theta)$ values of McConkey and Preston. However, the largest scattering angle covered by them is 90°, while for the present work $\sigma(\mathrm{He}, \theta)$ values were needed for angles up to 130°. Therefore, in our laboratory, relative values of $\sigma(\mathrm{He}, \theta)$ for scattering angles of 60° to 135° were measured[10] and were normalized to the absolute values of McConkey and Preston in the overlapping angular region of 60° and 90°. These normalized values were used to extend the angular range of McConkey and Preston to 135°.

Our primary measurements are the ratios $\sigma(\mathrm{HCN}, \theta)/\sigma(\mathrm{He}, \theta)$, and we present these values in Table I. Multiplication of these DCS by the $\sigma(\mathrm{He}, \theta)$ measurements of various authors described above gives the absolute DCS $\sigma(\mathrm{HCN}, \theta)$, which we present in Table II. Because of the present uncertainty in the $\sigma(\mathrm{He}, \theta)$ values themselves, we note that the DCS in Table II and σ_I and σ_M in Table III (see below) may be susceptible to changes when more reliable values of $\sigma(\mathrm{He}, \theta)$ become available in the future. The errors in $\sigma(\mathrm{HCN}, \theta)$ values are estimated to be ± 23% at 3 eV, ± 11% at 5 and 11.6 eV, and ± 18% at 21.6 and 50 eV. They are the square roots of the qua-

TABLE II. Differential elastic electron scattering cross sections σ(HCN, θ) (10^{-20} m^2/sr). Estimated errors in these measurements are ± 20% at 3 eV, ± 11% at 5 and 11.6 eV, and ± 18% at 21.6 and 50 eV electron impact energies.

θ (deg) \ E_0 (eV)	3	5	11.6	21.6	50
20	7.9	5.2	5.5	3.4	2.7
30	4.0	2.9	2.9	1.8	1.1
40	3.0	2.2	1.9	1.1	0.53
50	2.4	1.7	1.3	0.62	0.27
60	1.6	0.96	0.84	0.43	0.16
70	1.2	0.89	0.55	0.25	0.10
80	1.1	0.87	0.48	0.19	0.089
90	0.94	0.88	0.47	0.20	0.077
100	0.84	0.88	0.50	0.24	0.092
110	0.89	0.91	0.54	0.26	0.10
120	1.0	0.96	0.56	0.32	0.19
130	1.3	1.1	0.72	0.54	0.27

dratic sums of the ± 10% error in the ratio measurements and the error in the σ(He, θ) values. Andrich and Bitsch[7] estimate ± 20% error at 3 eV and ± 5% error at 5 and 11.6 eV in their values of σ(He, θ). McConkey and Preston[8] quote an error of ± 15% at 21.6 and 50 eV electron impact energies.

Final differential cross sections of HCN[σ(HCN, θ)] are plotted in Figs. 1–3, where they are compared with the results of the Born approximation[12] and of the semiclassical perturbation theory of Dickinson.[13] The agreement of the present results with the Born theory is fairly satisfactory even at scattering angles as large as 20° (Figs. 1–3). At the electron impact energies of 3 and 5 eV and at the scattering angle of 20°, the measured values are lower and are within about a factor of 2.5 of the Born predictions. At 11.6 eV, the agreement is excellent and may be fortuitous. At 21.6 and 50 eV and at 20° scattering angle, the measured values are higher and are within about a factor of 2 of the Born predictions.

At larger scattering angles ($\theta > 20°$). Born results are not expected to be accurate. However, classical perturbation theory[13] for a fixed point-dipole potential can be used to calculate differential cross sections at intermediate angles. There is an upper bound to the scattering angle beyond which the classical model is doubtful. In Figs. 1–3 the results of this theory are plotted as dashed lines, and the angular region in which results

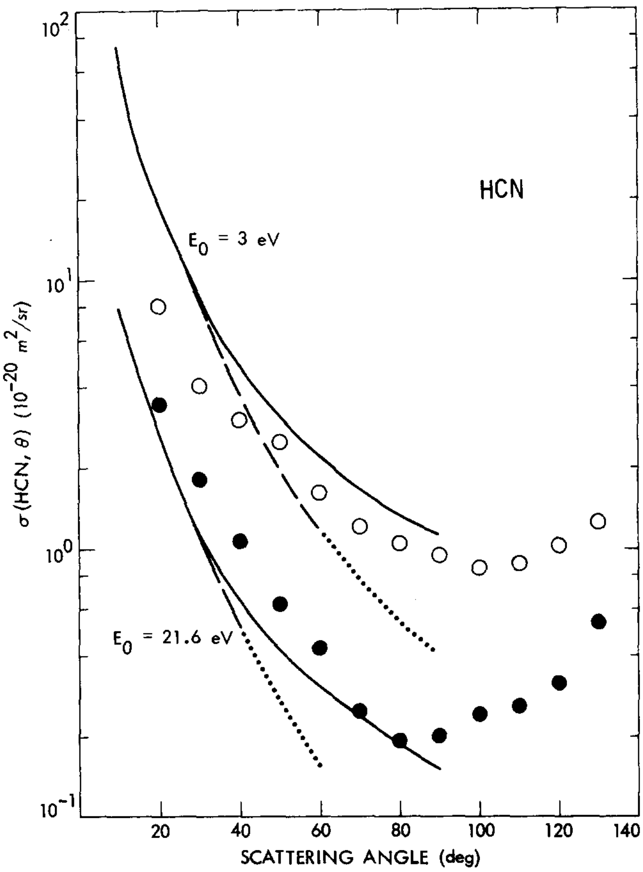

FIG. 1. Differential elastic cross sections of HCN at electron impact energies of 3 and 21.6 eV. Solid lines represent Born results; dashed lines extended by dots are calculations in the classical perturbation theory of Dickinson. Results of this theory are doubtful for the dotted extensions. o —Results of present measurements at 3 eV obtained by using helium elastic cross sections of Andrick and Bitsch. ●—Results of present measurements at 21.6 eV obtained by using helium elastic cross sections of McConkey and Preston.

have been plotted, but are not expected to be valid, are indicated by the dotted extensions.

Table III shows integral σ_I and momentum transfer σ_M cross sections. These cross sections were calculated from the following relations:

$$\sigma_I = 2\pi \int_{\theta_1}^{\theta_2} \sigma(\mathrm{HCN}, \theta) \sin\theta \, d\theta, \tag{4}$$

TABLE III. Integral σ_I and momentum transfer σ_M cross sections in units of 10^{-20} m^2 at various electron impact energies E_0 (eV). σ_I^* and σ_M^* are the integral and momentum transfer cross section values, respectively, between scattering angles of 0° and 20°. They have been calculated from the Born approximation normalized to the present results at 20°. σ_I and σ_M between 130° and 180° scattering angles have been obtained by extrapolation.

E_0 (eV)	σ_I^* (0°–20°)	σ_I (20°–130°)	σ_I (130°–180°)	σ_I (0°–180°)	σ_M^* (0°–20°)	σ_M (20°–130°)	σ_M (130°–180°)	σ_M (0°–180°)
3	35 ± 8	16 ± 3	4.2 ± 1.0	55 ± 14.4	0.12 ± 0.03	9.9 ± 2.3	7.7 ± 2.3	18 ± 4.4
5	36 ± 4	13 ± 2	3.2 ± 0.6	52 ± 7.8	0.13 ± 0.01	8.5 ± 0.9	5.8 ± 1.2	14 ± 2.2
11.6	41 ± 5	9.4 ± 1.0	2.4 ± 0.5	53 ± 7.9	0.13 ± 0.02	5.4 ± 0.6	4.4 ± 0.9	9.9 ± 1.5
21.6	27 ± 5	5.1 ± 0.9	3.1 ± 0.8	35 ± 7.4	0.075 ± 0.014	2.8 ± 0.5	5.9 ± 1.5	8.8 ± 1.8
50	23 ± 4	2.6 ± 0.5	2.7 ± 0.7	28 ± 5.9	0.059 ± 0.011	1.3 ± 0.2	5.1 ± 1.3	6.5 ± 1.4

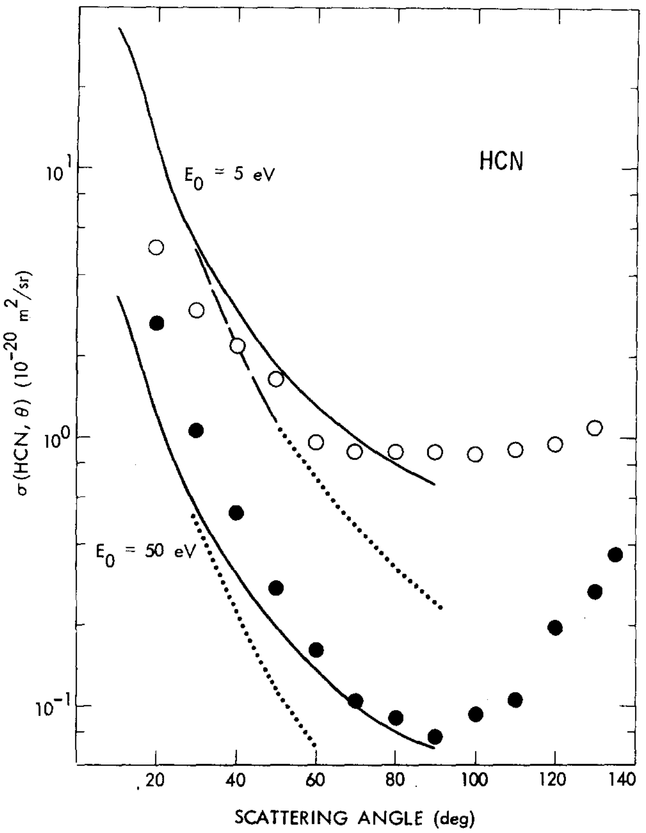

FIG. 2. Differential elastic cross sections of HCN at electron impact energies of 5 and 50 eV. The rest is the same as in Fig. 1.

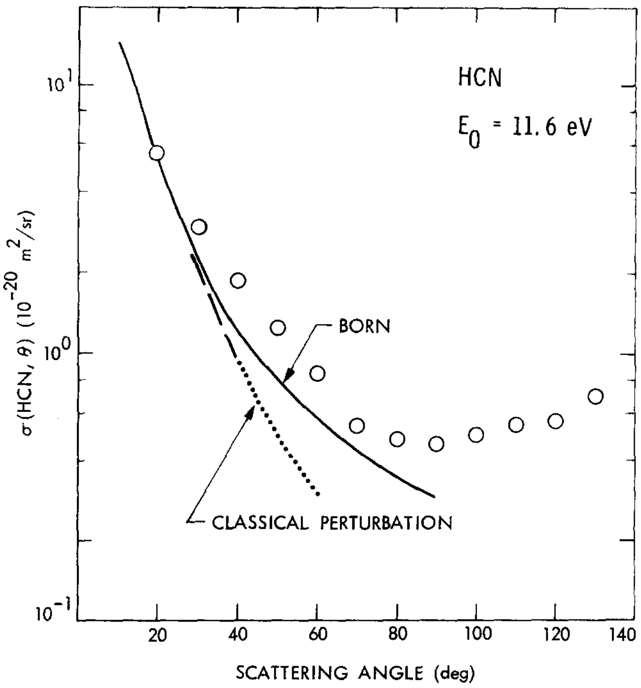

FIG. 3. Differential elastic cross sections of HCN at an electron impact energy of 11.6 eV. The rest is the same as in Fig. 1.

and

$$\sigma_M = 2\pi \int_{\theta_1}^{\theta_2} \sigma(\mathrm{HCN}, \theta) \sin\theta(1-\cos\theta)\, d\theta, \qquad (5)$$

where θ_1 and θ_2 are lower and upper limits, respectively, of scattering angles within which the integration is performed. In the present work, σ(HCN, θ) values between 20° and 130° were measured. However, due to experimental difficulties, accurate measurements in angular regions of 0° to 20° and 130° to 180° could not be carried out. Therefore, σ(HCN, θ) values in these regions were obtained by extrapolations. We used the shape of the DCS curve between 0° and 20° predicted by the Born approximation to extrapolate the present measurements below 20° scattering angle. At present, theoretical results for angles larger than 130° are not available. Therefore, 120° and 130° data points were joined by a straight line. This straight line was then extended to 180° to obtain σ(HCN, θ) values between 130° and 180°. In Table III, contributions from each angular region are shown separately. The errors associated with σ_I and σ_M for 20° to 130° angular region are also shown. However, it is very difficult to give any accurate estimate of errors associated with these cross sections for 0° to 20° and 130° to 180° angular regions. In Table III we present estimated errors for these extrapolated regions which were obtained on the basis of errors associated with the 20° to 130° angular region. In the case of integral cross sections, most of the contribution to σ_I(0° to 180°) comes from the angular region of 0° to 20°. The values of σ_I (130° to 180°) are small and therefore do not significantly contribute to the total error. In the case of momentum-transfer cross sections, however, the region between 130° and 180° is important. For example, the σ_M(130° to 180°) values are comparable to and at 21.6 and 50 eV are larger than σ_M(20° to 130°). Therefore, any error in the extrapolation can produce a significant error in the momentum transfer cross sections σ_M(0° to 180°).

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