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Low-energy electron scattering with H_2O and NH_3 molecules

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Calculated total, differential, and momentum-transfer cross sections are reported for the vibrationally elastic scattering of electrons from H_2O and NH_3 molecules in the range of energy 0.5–20 eV. The total cross sections are approximated by a sum of the rotationally elastic ones and the rotational transition from ground to first excited state ($00 \rightarrow 10$). The first-order Born approximation with the rotating-molecule model is used in the calculation of the first rotational excitation cross section. The experimental value of the dipole moments of H_2O and NH_3 are used in this step of the calculation. Spherically approximate molecular wave functions are applied to calculate the spherical part of the interactions of the incident electron with the molecule and the rotationally elastic-scattering cross section, in which the static and exchange interactions are calculated exactly within the accuracy of the molecular wave function and a parameter-free correlation-polarization potential is used to account for the polarization effect. The agreement of the differential cross sections with the experimental data is good at small angles and reasonably good at intermediate and large angles. Good agreement with measured values is obtained for the momentum-transfer cross sections. Total cross sections are reported with theoretical results on the e-NH_3 system below 10 eV. The possible sources of the discrepancies between the current theoretical and experimental results are analyzed for the total cross sections at very low energies by a quantitative consideration of the contributions of very strong forward scattering at near-zero angles to the total cross sections.

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I. INTRODUCTION

The cross sections of e-H_2O and e-NH_3 scattering are very important in many fields of research, including space science, radiation physics, gas laser, and even fundamental chemistry. The scattering of electrons by H_2O has been studied extensively in both theory and experiment, but only a few studies have been carried out on the scattering of e-NH_3. The studies before 1986 were reviewed in detail by Gianturco and Jain [1]. In recent years a few measurements and *ab initio* calculations have been made on the differential, momentum-transfer, and total cross sections of these scattering processes. Elastic-differential and momentum-transfer cross sections of H_2O were calculated by Brescansin *et al.* [2] for collision energies from 2 to 20 eV using the Schwinger variational approach in fixed-nuclei (FN) static-exchange approximation. In their calculations the exchange interaction is treated exactly within the accuracy of the used target wave function, but the polarization effect was omitted completely. Because of the FN approximation, only the momentum-transfer and the differential cross sections at intermediate and large angles were obtained in their studies. A local exchange potential and a polarization potential were used by Gianturco and Scialla [3] in the FN approximation with a correction via a Born closure formula to the well-known divergence in the forward scattering. The continuum multiple-scattering (CMS) method was applied by Sato, Kimura, and Fujima [4] to obtain differential and momentum-transfer cross sections. They adopted a hybrid S-matrix approach to correct the divergence of the FN approximation at small angles. However, the total cross sections were not reported by Gianturco and Scialla or by Sato, Kimura, and Fujima, although in their calculations corrections were made for the FN approximation. In the earlier studies of Jain and Thompson [5], the first rotational excitation ($00 \rightarrow 10$) was included; and total, differential and momentum-transfer cross sections were calculated.

The fixed- and adiabatic-rotation approximation was used by Jain and Thompson [6] in the earlier *ab initio* calculations of e-NH_3 scattering. Local exchange and a parameter-free polarization potential were applied to produce the momentum-transfer cross sections. Most recently, Pritchard, Lima, and McKoy [7] applied the FN static-exchange approach to the differential and momentum-transfer cross sections. Exchange was calculated completely within the accuracy of the molecular wave function.

Several experiments have been carried out in recent years. The differential cross sections were measured by Danjo and Nishimura [8] and Shyn and Cho [9] for the e-H_2O scattering process. The total cross sections of H_2O and NH_3 molecules were measured by Sueoka, Mori, and Katayama [10], Nishimura and Yano [11], and Szmytkowski *et al.* [12]. The measurements for the momentum-transfer cross sections were summarized by Itikawa [13] and Hayashi [14]. The experimental results reported in recent years make it possible to make a direct comparison between theory and experiment and examination about the adequacy of the theoretical methods. The differential cross sections of the measurements have been reproduced reasonably well in the recent calculations. But the measured total cross sections have not been explained in any theoretical studies. At the energies below 10 eV the experimental data [10,11,14] were much smaller than the earlier calculated results of Jain and Thompson [5].

In this paper we present the results of our calculations for the cross sections of electron scattering from H_2O and NH_3 molecules at energies from 0.5 to 20 eV. The calculations have been performed in a simple theoretical formalism. The molecular electronic states are approximated by spherical wave functions. The spherical part of the interactions of incident electrons with the targets are evaluated using approximate spherical molecular wave functions and the long-range multiple interactions are accounted for by a dipole potential. The spherical molecular wave functions are obtained with a self-consistent-field method. The rotationally elastic cross sections are obtained by solving the scattering of electrons in the isotropic fields of the spherical interactions, in which static and exchange interactions are calculated exactly within the accuracy of the molecular wave functions and the polarization effect is considered by a parameter-free correlation-polarization (CP) potential. The rotational excitation cross section of $00 \rightarrow 10$ transition is evaluated from a rotating-molecule model with just a long-range dipole potential using the first-order Born approximation. The total vibrationally elastic cross sections are approximated by incoherent sums of the pure elastic and the first rotational excitation cross sections calculated separately from the spherical interaction and the long-range dipole potential. Generally good agreement is obtained for the differential and momentum-transfer cross sections compared with the measured values. Five sets of total cross sections are given, which are, respectively, the pure elastic total cross sections, the vibrationally elastic total cross sections with and without the small-angle scattering in the range of $0°-1°$, $0°-5°$, and $0°-10°$ being neglected. In this way the contribution of the small-angle scattering to the total cross section can be shown clearly. By noting the fact that the omission of the small-angle scattering is an important source of the uncertainties in measurements on total cross sections, a possible source of the discrepancies of total cross sections between the theoretical predictions and the reported experimental results are analyzed with emphasis on the difference between theory and experiment resulting from the inclusion of small-angle scattering in total cross sections.

The present method has some similarities with the method used by Jain [15], but Jain's calculations were performed at energies higher than 10 eV. The results of the present calculations will show that application of the present approach at such low energies is adequate.

II. THEORY

A. Spherical approximate molecular wave function

In the Born-Oppenheimer approximation, making a multiple expansion around the central nuclei (O or N) for the interaction of electrons with nuclei, we have for the electronic Hamiltonian

$$\begin{aligned}\hat{H} &= \sum_i -\tfrac{1}{2}\nabla_i^2 + \sum_{i,j}\frac{1}{r_{ij}} - \sum_{\mu,i}\frac{Z_\mu}{r_{\mu i}} \\ &= \sum_i -\tfrac{1}{2}\nabla_i^2 + \sum_{i,j}\frac{1}{r_{ij}} \\ &\quad - \sum_{\mu,i}\sum_l \left[\frac{4\pi Z_\mu}{2l+1}\right]\frac{r_<^l}{r_>^{l+1}}\sum_{m=-l}^{l} Y_{lm}^*(\hat{\mathbf{r}}_i)Y_{ml}(\hat{\mathbf{R}}_\mu)\ ,\end{aligned} \tag{1}$$

in which i and μ run, respectively, over the electrons and nuclei; Z_μ is the nuclear charge; $\mathbf{r}_i$ and $\mathbf{R}_\mu$ are, respectively, the ith electronic and μth nuclear space coordinates centered on the central nucleus (O or N). Retaining only the first term in the expansion of (1), a spherical model Hamiltonian $\hat{H}_0$ is obtained

$$\hat{H}_0 = \sum_i -\tfrac{1}{2}\nabla_i^2 + \sum_{i,j}\frac{1}{r_{ij}} - \sum_{\mu,i}\frac{Z_\mu}{r_>}\ , \tag{2}$$

where $r_>$ is the larger of r_i and R_μ. The neonlike spherical approximate molecular wave functions and electron densities are solved with the model Hamiltonian (2) using the numerical Hartree-Fock method. Because of the electronic situation from the molecular structure point of view, i.e., hydrogen atoms around a heavy nucleus, the spherical approximation is feasible in molecular electron-state calculations. The expected values of the exact Hamiltonian (1) with the spherical wave function are -75.66 and -55.66 hartree, respectively, for H_2O and NH_3, which are very close to the Hartree-Fock values without spherical approximation.

B. Electron scattering

The rotationally elastic scattering of the incident electrons by the spherically approximated target core is calculated by partial-wave expansion with exact exchange and a parameter-free CP potential

$$\left[\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} - 2V_s(r) - 2V_{\mathrm{CP}}(r) + k^2\right]u_l(r) = K_l u_l(r)\ , \tag{3}$$

in which V_s, V_{CP}, and $K_l u_l(r)$ are calculated using the spherical molecular wave function. V_s is the static potential, V_{CP} is the parameter-free CP potential following Padial and Norcross [16]. The exchange kernel $K_l u_l(r)$ is calculated exactly within the accuracy of the molecular wave function without local approximation.

The long-range interaction of the polar target is taken into account by the second term in the expansion of the interaction of incident electron with the nuclei in target, which is similar to that in Eq. (1)

$$V_{\mathrm{dipole}}(\mathbf{r}) = C\frac{r_<}{r_>^2}P_1(\cos\theta)\ , \tag{4}$$

where the scaling factor C is chosen so that V_{dipole} has the correct asymptotic value in the long-interaction range. Therefore

$$V_{\text{dipole}}(\mathbf{r})=\begin{cases}\dfrac{r}{R_\mu^3}DP_1(\cos\theta), & r<R_\mu\\ \dfrac{D}{r^2}P_1(\cos\theta), & r>R_\mu\end{cases} \tag{5}$$

where $D(=0.728$ a.u. for H_2O and 0.578 a.u. for NH_3, respectively) is the permanent dipole moment of the target. The dipole potential (5) is finite at the zero point of r without any empirical cutoff function, which is currently applied to remove the infinity of the dipole potential near $r=0$.

The rotational excitation from ground to first excited state $(00\rightarrow10)$ induced by the dipole potential (5) is calculated by employing the Born approximation with just the dipole potential for the rotating molecule [17].

III. RESULTS

Three sets of differential cross sections (DCS's), the rotationally elastic, the first rotational transition, and the sum of them, are displayed in Fig. 1 with experimental data. The results without CP potential are also presented. The dominance of the $00\rightarrow10$ transition at small scattering energies can be seen clearly. Below 5 eV the small-angle scatterings, which are mainly scattered from higher partial waves and where the Born approximation works well for quite low energies, predominate the scattering process. At 0.5 eV almost 50% of the scattered electrons come from the small-angle scattering at less than 1°, and these scatterings are generally very difficult to distinguish from the incident electron beam in experiment. The predictions of the Born approximation are reliable for such small scattering angles. Therefore we can make a quantitative estimate of the contributions of small-angle scattering to the total cross section. In this way it is found that at 2 eV the contribution of the scattering in the range of 0°–1° to the total cross section is 23 Å^2, while the recommended value of the total cross section by Hayashi [14] is only 19 Å^2. At this energy the scatterings less than 5°, 10°, and 15°, respectively, contribute about 37, 42, and 46 Å^2 to the total cross section. From this point of view, at such low energies the underestimated small-angle scattering in the experiments might be one important source of the discrepancies between the current theoretical predictions and the experimental measurements for the total cross sections.

For energies above 10 eV, the rotationally elastic scattering by the spherical interaction of the target plays a more important role in the scattering process and predominates the scattering at intermediate and large angles. At 20 eV the scattering by the spherical part of the interaction alone can give reasonably good scattering parameters and predominate the total cross section. Due to the molecular structure of H_2O and NH_3, a few hydrogen nuclei around a heavy nucleus (O or N), retaining only the first term in the one-center expansion of Eq. (1) is feasible for the calculation of the spherical part of the interaction. The applications of this approach to CH_4 and SiH_4 have been given [18]. For these reasons fairly good predictions for the DCS at intermediate and large angles are obtained by the present calculations at the plotted energies. The main features of the measured DCS, i.e., the shoulder near 70° and the minimum point near 120°, are reproduced qualitatively. The present DCS's agree well with calculations without the spherical approximation for the core interactions [2,7] at intermediate and large angles except for the too deep minimum point in the present results, due to the neglect of the transitions to higher rotational excitation states and their coupling with each other. Particularly, the present predictions for the backward-scattering amplitude agree well with other calculations [2,7], for which higher values for H_2O at 165° were also given by Shyn and Cho by extrapolating the DCS's from smaller angles.

The CP potential plays an important role at energies below 10 eV in the pure elastic scattering. The difference between the pure elastic DCS's with and without the CP potential is drastic at the plotted energies below 10 eV for the angles less than 90°. Because the CP potential actually has long-interaction range, the drastic effects on the DCS's at small scattering angles can be understood. At energies of 15 and 20 eV and angles larger than 30°, the effects of the CP potential are small, and the results with and without CP potential agree well with each other. The present static-exchange results without CP potential are in reasonably good agreement with those of Refs. [2] and [7] at 10, 15, and 20 eV. One can believe that the present spherical model works well at these higher energies.

The total cross sections are shown in Fig. 2 with five sets of the present results and a few sets of experimental data. Five sets of the present data are, respectively, the rotationally elastic cross section and the total cross section with and without the exclusion of the small-angle scattering at less than 1°, 5°, and 10°. The results without CP potential are also displayed in Fig. 2. The main question for the total cross sections is why all the measurements gave data much smaller than what was theoretically predicted; for example, the result obtained by Jain and Thompson [5] at energies below 10 eV. The experimental data plotted in Fig. 2 are, respectively, of Sueoka, Mori, and Katayama, using a time-of-flight (TOF) method without accounting for the systematic uncertainties due to forward scattering; Shyn and Cho, using a modulated cross-beam method and integrating the DCS from 10° to 165°; Nishimura and Yano, using an electron transmission device; and Szmytkowski *et al.*, using a linear transmission technique. However, except for the experiment of Szmytkowski *et al.*, none of the mentioned experiments has clarified the uncertainties due to the very-small-angle forward scattering. As we noted in the preceding paragraph, the small-angle scattering predominates the scattering processes at low energies. Quantitative comparisons between theory and experiment require considerations of the small-angle scatterings. Since the underestimation of the total cross sections in the experimental results is not definitely determined, we give five sets of total cross sections, in which the small-angle

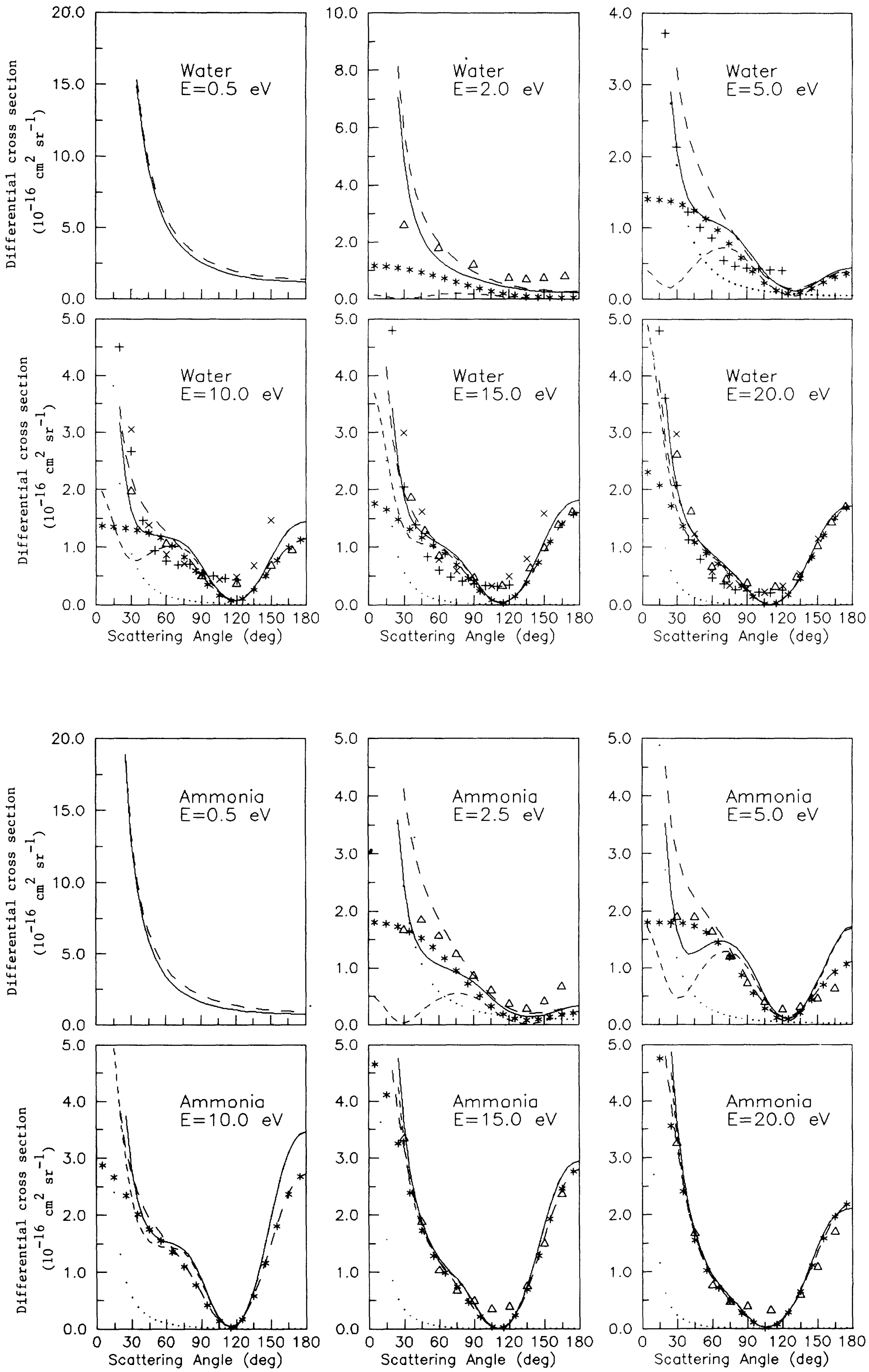

FIG. 1. Differential cross sections (in 10^{-16} cm^2 sr^{-1}). Present results: solid line, total DCS with CP potential; long-dashed line, total DCS without CP potential; dots, first-order Born rotational transition 00→10; short-dashed line, rotationally elastic DCS with CP potential; $*$, rotationally elastic DCS without CP potential; Δ, FN static-exchange results of Brescansin *et al.*, Ref. [2], for H_2O and of Pritchard, Lima, and McKoy, Ref. [7], for NH_3; $+$, experimental data of Danjo and Nishimura, Ref. [8]; $\times$, experimental data of Shyn and Cho, Ref. [9]. Note that at energies lower than 5 eV the total DCS is dominated by the 00→10 transition.

scattering is omitted to varying degrees. By noting the fact that the uncertainties of small-angle scattering in one set of experimental data are not the same for different energies and assuming that the smaller the scattering energy the more the underestimation of the small-angle scattering, we can interpret qualitatively the plotted experimental data, especially the minimum structure around 5 and 3 eV, respectively, for H_2O and NH_3, which cannot be reproduced by theory if the small-angle scattering is not excluded, as in the first set of the present results and the results of Jain and Thompson. The experimental result of Sueoka, Mori, and Katayama is reproduced well by the present calculation when the small-angle scattering within 10° is excluded from the total cross sections. But it has to be noted that generally the small-angle scattering cannot be excluded with the same degree for different energies. Therefore the comparison of the present result with that of Sueoka, Mori, and Katayama is only of qualitative significance. In the measurements of Szmytkowski *et al.* [12] and Szmytkowski [19], the small-angle scattering was considered qualitatively. They estimated the incomplete discrimination of the small-angle scattering using the DCS's at 0° and at an estimated solid angle. The DCS used by them was obtained by extrapolating the experimental DCS at finite angles. But the contribution of the small-angle scattering to the total cross section was underestimated significantly. Only 0.4–1 % of the total cross section was assigned to the small-angle scattering with the solid angle of 3×10^{-3} sr. While the present calculations show that the small-angle scattering, even in the range of 0°–1°, which corresponds to about 1×10^{-3} sr, takes a much more important role at these energies. To make a quantitative comparison be-

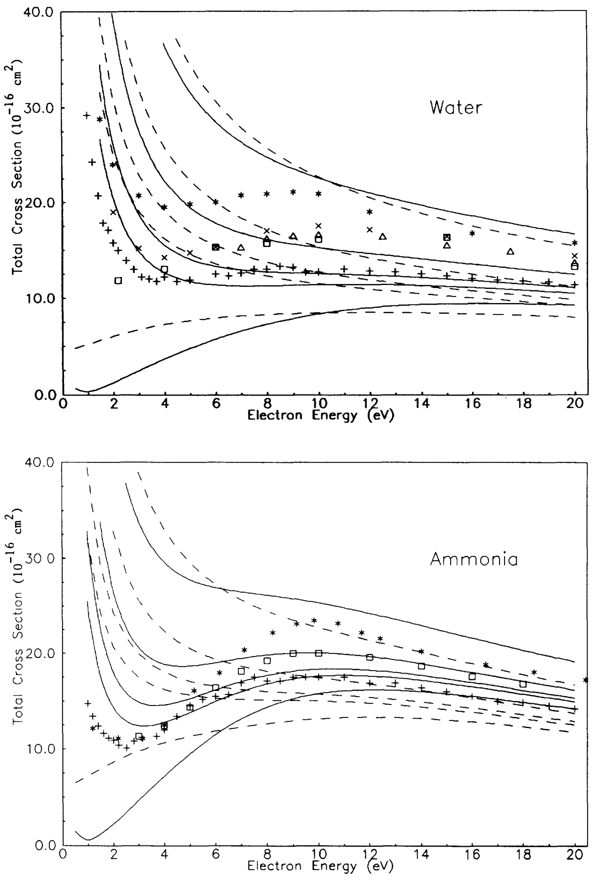

FIG. 2. Total cross sections (in 10^{-16} cm^2). Present results: five solid lines, from top to bottom, are respectively, the total cross sections with no small-angle scattering, 0°–1° small-angle scattering, 0°–5° small-angle scattering, 0°–10° small-angle scattering being neglected; and the rotational elastic cross section. The five dashed lines are the same as the solid lines but without the CP potential. Experiment of H_2O: +, Sueoka, Mori, and Katayama, Ref. [10]; ✱, Szmytkowski, Ref. [19]; ×, Hayashi, Ref. [14]; □, Shyn and Cho, Ref. [9]; Δ, Nishimura and Yano, Ref. [11]. Experiment of NH_3: +, Ref. [10]; ✱, Szmytkowski *et al.*, Ref. [12]; □, Bruche, Ref. [20].

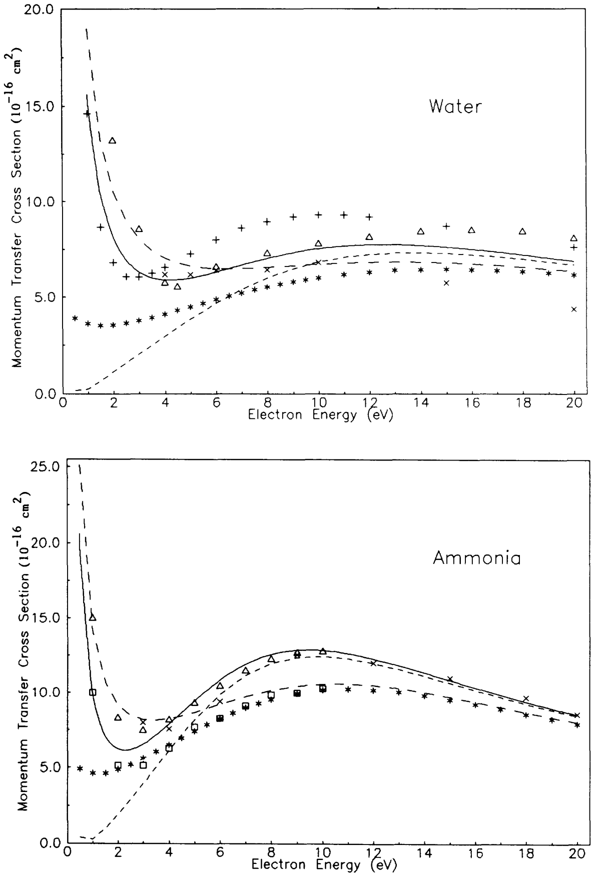

FIG. 3. Momentum-transfer cross sections (in 10^{-16} cm^2). Present results: solid line, the total momentum-transfer cross sections with CP potential; long-dashed line, total momentum-transfer cross sections without CP potential; short-dashed line, rotationally elastic data with CP potential; ✱, rotationally elastic data without CP potential. Other results of H_2O: Δ, FN static-exchange of Brescansin *et al.*, Ref. [2]; +, experimental data of Hayashi, Ref. [14]; ×, experimental data of Danjo and Nishimura, Ref. [8]. Other results of NH_3: ×, FN static-exchange result of Pritchard, Lima, and McKoy, Ref. [7]; Δ, fixed- and adiabatic-rotation approach of Jain and Thompson, Ref. [6]; □, experimental data of Itikawa, Ref. [13].

tween theory and experiment, the small-angle scattering must be considered carefully in the measurement for the total cross sections.

The considerable effects of the CP potential on the pure elastic scattering can also be seen in Fig. 2. Without the CP potential the Ramsauer-Townsend (RT)-type minimum structure cannot be produced in the rotationally elastic cross sections as well as in the total cross sections even if the small-angle scattering less than 10° is removed. The CP potential has a relatively small effect at energies above 10 eV.

The momentum-transfer cross sections are plotted in Fig. 3. The momentum-transfer cross sections are not very sensitive to the small-angle scattering and may have more direct significance than the total cross sections in practical applications. Both theoretical and experimental results have been reported for H_2O as well as NH_3 molecules. Making a comparison of the present results with others can make a direct examination of the adequacy of the theoretical approach. At 4 eV, more than 50% of the momentum-transfer cross sections come from the rotationally elastic core scattering, while at the same energy only about 10% of the total cross sections are contributed by the core scattering if the small-angle scattering is not excluded from the total cross sections. So we can expect that the core interactions determine the momentum-transfer cross sections at energies higher than 4 eV. Comparison of the present results at these energies with the measured data and other calculations will provide information about the accuracy of the present core interactions and the DCS at intermediate and large angles. It is shown that the present results of e-H_2O scattering agree well with the recommended values of Hayashi [14], which were determined by analyzing the experiments of electron scattering and the parameters of swarm electrons. The present results of e-NH_3 scattering agree well with the recommended data of Itikawa [13] below 6 eV and with the static-exchange results of Pritchard, Lima, and McKoy [7], and Jain and Thompson [6] at higher energies. At 20 eV, 6.7 Å^2 of the 6.9 Å^2 total momentum-transfer cross section come from the rotationally elastic scattering. So at this energy the momentum-transfer cross section is almost completely determined by the rotationally elastic scattering and the spherical part of the interaction.

The effects of the CP potential on the momentum-transfer cross sections are also important below 5 eV. Because the present DCS's are much lower than the static-exchange values of Refs. [2] and [7] around the minimum point at 120°, the present momentum-transfer cross sections without CP potential are generally lower than their values at energies above 6 eV.

In conclusion, a simple but adequate theoretical approach is used in the present studies of the scattering of low-energy electrons from H_2O and NH_3 molecules. The importance of the small-angle scatterings in the interpretation of the measured total cross sections is demonstrated by definite numerical calculations and comparisons. It has been shown that the reported experimental data for the total cross sections might have underestimated the small-angle scattering at small scattering energies. The momentum-transfer cross sections of the present calculations agree well with measurements and other *ab initio* calculations. The main sources of error in the present calculations are the spherically approximate core interactions, the neglected transitions to higher rotational excitation states, and the Born approximation for the dipole transition of 00→10. Because of the special molecular structure of H_2O and NH_3, the spherical approximation for the core interactions is reasonably good, and it has been demonstrated by the momentum-transfer cross sections and DCS at intermediate and large angles. The cross sections of transition to higher rotational states are very small compared with the dipole transition 00→10, and the neglect of these transitions will not induce considerable error in the range of energy concerned, except the minimum value in the DCS. The Born approximation is suitable for the small-angle scattering, so application of the Born approximation for the rotational transition is adequate for the main purpose of the present calculations—analyzing the importance of small-angle scattering in the interpretation of the experimental total cross sections. Further experiments with considerations for the small-angle scattering are needed for definite quantitative comparison between theory and experiments.

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