The free–free absorption coefficients of the negative ion of molecular hydrogen in the far-IR spectrum

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ABSTRACT
Accurate momentum transfer cross-sections from experimental and theoretical sources are used to calculate H$_2^-$ free–free absorption coefficients at far-IR wavelengths. We include results from recent theoretical computations for vibrational motion of the molecular nuclei.

Key words: molecular data – molecular processes – stars: atmospheres – infrared: general.

1 INTRODUCTION
The negative ion H$_2^-$ is the most important molecular contributor to continuous opacity in the atmospheres of late-type stars. It becomes a significant source in low-temperature stars, particularly in M stars, where hydrogen is sufficiently abundant in molecular form to play a substantial role. The lack of any stable bound states for H$_2^-$ (see Massey 1976) results in the free–free mechanism being solely responsible for continuous absorption by this negative ion. Free–free transitions are known to have their greatest efficiency as absorbers in the IR range, and, in the present paper, we shall confine consideration to this region of the spectrum. Our knowledge of radiative transitions of H$_2^-$ comes exclusively from theoretical investigations. Ab initio calculations by Bell et al. (1975) and Bell (1980), based on the close-coupling method, showed that computations by Sommerville (1964) underestimated H$_2^-$ coefficients by over 60 per cent in the far-IR. Bell (1980), in the most sophisticated calculation to date, used a two-centre wavefunction expansion; these coefficients were over 30 per cent larger at low temperatures than earlier close-coupling results. Other estimates of H$_2^-$ absorption have been based on approximations for radiative dipole matrix elements (John 1975, 1978). These formulae depend on asymptotic properties of wavefunctions of the electron undergoing transitions. Both formulae reduce to the same expression in the low-frequency limit, providing 'exact' numerical values for matrix elements in this case. In the first of these computations, John (1975) used the method of Dalgarno & Lane (1966), in which matrix elements are expressed in terms of momentum transfer cross-sections. Sommerville (1964) used a similar approximation, with the momentum transfer cross-sections replaced by their elastic scattering counterparts; these matrix elements, however, do not have the correct behaviour in the soft-photon limit. The second formula (John 1978) was based on a method by John (1966), which used scattering phase shifts of continuum states. Both methods gave results in reasonable accord with each other at low photon energies. Coefficients determined from momentum transfer cross-sections were in very good agreement with the two-centre results of Bell (1980) in the far-IR.

Advances in understanding free–free transitions of atomic and molecular systems have always been associated with developments in the corresponding electron–atom or electron–molecule systems. Recent studies of electrons interacting with molecules at low energies have resolved some of the uncertainties and divergences between the scattering cross-sections obtained by various experimental groups, and between the results of theory and experiment. Molecular hydrogen, one of the simplest molecules to treat theoretically, has been one of the most fruitful cases explored. The crossed-beam technique is one of the most accurate means of measuring cross-sections directly. The angular distribution of scattered electrons, and its functional dependence on energy, provides the most sensitive test of accord between theory and experiment. The work of Brunger et al. (1991) and Buckman et al. (1990) has provided the closest agreement between theory and experiment in low-energy e + H$_2$ scattering so far. The theoretical work used in this comparison took into account vibrational, as well as rotational, motion of the molecular nuclei and the polarization of the target. These cross-sections were in satisfactory agreement with earlier beam experiments, and in good agreement with cross-sections derived indirectly by an analysis of swarm observations (Englund et al. 1988; Buckman & Phelps 1985).

Because H$_2^-$ free–free absorption in the far-IR spectrum can be determined directly from momentum transfer cross-sections, it is timely to consider the effects of recent theoretical and experimental research into e + H$_2$ systems on these absorption coefficients.
2 METHOD OF COMPUTATION

Absorption coefficients in the IR spectrum for the free-free transitions of the negative ion of molecular hydrogen, at temperature $T$ (K) and wavelength $\lambda$ (\textmu m), can be expanded as follows.

$$K_\lambda^J(T) = \lambda^2 A(T) + \sum_{n=0}^{\infty} \lambda^{-n} B_n(T) \quad (\text{cm}^4 \text{dyn}^{-1}),$$

where

$$A(T) = 140 \ T^{-7/2} \int_0^{\infty} \exp(-cE) E^2 Q_m(E) \, dE$$

$$+ \left( \frac{c}{11605/T} \right).$$

The coefficients defined by equations (1) and (2) have been averaged over a Maxwellian distribution function and include the stimulated emission factor; they are expressed in units per unit electron pressure, per neutral hydrogen molecule. $Q_m(E)$ is the momentum transfer cross-section for the $e + H_2$ system (in units of $10^{-18}$ cm$^2$) and $E$ is the energy of the electron projectile (given in eV). In the far-IR, terms involving the series of functions $B_n(T)$ can be ignored. From the results of Bell et al. (1975) and Bell (1980), we found that values of the parameter $\epsilon$ [= 460/(4AT)] gave a rough guide to the inaccuracies resulting from the omission of the $B_n(T)$ terms; errors are less than 5 per cent for $\epsilon$ smaller than 0.05, and are below 10 per cent for $\epsilon$ less than 0.1.

Neglect of the terms $B_n(T)$ results in a simple power law of $\lambda^2$ for the wavelength behaviour of $H_2$ free-free absorption coefficients; their temperature dependence rests on how the momentum transfer cross-section $Q_m(E)$ varies with energy. The exponential factor arising from Maxwellian averaging ensures strong weighting of the coefficients to lower-energy molecular cross-sections and smooths out differences between alternative sets of data.

The analysis of a swarm of electrons drifting and diffusing through a neutral gas under an applied electric field provides a valuable experimental source of momentum transfer cross-sections. In their latest work, England et al. (1988) used a $H_2$-Ne mixture, which proved more sensitive to the 0–1 vibrational excitation cross-section for molecular hydrogen near threshold than did the mixtures $H_2$–He and $H_2$–Ar, used in earlier studies.

Differential cross-sections (DCS) provide the most comprehensive means of comparing theory with experiment. Crossed-beam observations of the vibrational excitation of $H_2$ near threshold, which show the widest disparity, provide the most sensitive case for comparison. Momentum transfer cross-sections for $e + H_2$ scattering derived from integrals of crossed-beam DCS have been given by a number of groups (Srivastava, Chutjian & Trajmar 1975; Shyn and Sharp 1981; Brunner et al. 1991). These data are only of limited value in computations of $H_2$ free-free absorption coefficients, as results are only available for energies of 1 eV and above, in which case absorption coefficients can only be evaluated with any confidence for temperatures above 5000 K. The precision of total elastic scattering, ro-vibration excitation and momentum transfer cross-sections derived by integrating DCS are suspect, owing to the need to estimate values for angular regions outside the scope of the measuring apparatus.

The theory of electron–molecule scattering is well reviewed in the literature (see, for example, Lane 1980; Morrison et al. 1987; Morrison 1988) and we confine discussion in this section to cases used to calculate free-free transitions of $H_2$. The earliest theoretical treatments of $e + H_2$ scattering assumed that the molecular target consisted of a rigid rotator with nuclei fixed at their equilibrium separation $R$ (usually taken as 1.4 au). Wavefunctions were expanded as products of the ground molecular target state $X^1\Sigma_g^+$ and free electron orbitals, in antisymmetrized combinations to allow for electron exchange; excited states were included via a local adiabatic polarization potential, determined semi-empirically, involving adjustable parameters. Massey & Ridley (1956) ignored polarization and used variational methods to compute $s$-wave phase shifts. Bell et al. (1975) included polarization in their research, but simplified the analysis so as to include only the ground rotational state of $H_2$ ($J = 0$), and omitted non-spherically symmetric terms in electron–molecule interactions. Hara (1969) and Bell (1980) used a two-centre method and prolate spheroidal coordinates, and restricted both static and polarization potentials to two-term expansions. Schneider (1975) and Collins, Robb & Morrison (1978) used the static–exchange approximation, which included non-spherical and spherical interaction terms and ignored polarization. Their analysis required an extended set of orbitals and Buttle's method of correcting R-matrices to ensure convergence. In recent work, Dr Morrison's group (University of Oklahoma) have allowed for vibrational motion of target nuclei, with the internuclear separation $R$ treated as a variable. In one approach, the static–exchange–polarization (SEP) method (Morrison et al. 1987), the motion of the projectile electron was given in terms of a local potential $V_{\text{SEP}}(r, \theta, R)$:

$$V_{\text{SEP}}(r, \theta, R) = V_{\text{SE}}(r, \theta, R) + V_{\text{EX}}(r, \theta, R) + V_{\text{ID}}(r, \theta, R).$$

$V_{\text{SE}}$, $V_{\text{EX}}$ and $V_{\text{ID}}$ refer to the static, exchange and polarization components, respectively, $(r, \theta)$ being the coordinates of the electron. Static terms arise from Coulomb forces between the projectile and the molecular target and are constructed from near-Hartree–Fock orbitals. The local exchange (FEG) potential is derived from a non-local exchange kernel by applying the free–electron–gas approximation for the molecular target electrons and the Born approximation for the scattering function. The polarization potential is based on the BTAD ("better than adiabatic dipole potential") method that includes target polarization, correlation and the effects of excited electronic molecular states. In this ab initio parameter-free method, the potential has the asymptotic form

$$V_{\text{ID}}(r, \theta, R) \sim -\alpha_0(R)/(2r^2) - \alpha_2(R) P_2(\cos \theta)/(2r^4).$$

Morrison et al. found that averages of the spherical and non-spherical target polarization components $\alpha_0(R)$, $\alpha_2(R)$ over ground vibrational states were in excellent agreement with experimental values and more elaborate molecular structure computations. The body-frame vibrational close-coupling method (BFVCC) offers further refinements over the SEP procedure, by treating nuclear vibration exactly through the inclusion of vibrational states in wavefunction expansions. These BFVCC results were used in the comparison of theoretical and crossed-beam elastic and ro-vibration DCS for the
e + H$_2$ system by Buckman et al. (1990) and Brunger et al. (1991), and successfully resolved discrepancies between theoretical and experimental results for vibrational excitation of H$_2$ near threshold; they also gave the best agreement of elastic scattering published so far. Modified effective range theory (MERT) (see Fabrikant 1984; Morrison 1988; Isaacs & Morrison 1992) was very useful in extrapolating momentum transfer cross-sections to the low energies required in free–free absorption computations. An application to e + H$_2$ scattering for the BFVCC case is given by Morrison & Isaacs; they find that the simple analytic formula

$$\begin{align*}
Q_m(E) &= 5.706 + 18.619\sqrt{E} + 6.6235\ E \ln E, \\
&\quad (10^{-16} \text{ cm}^2),
\end{align*}$$

(Morrison & Isaacs, private communication) gives BFVCC results to better than 0.7 per cent for energies below 0.1 eV. Morrison & Trail (private communication) and Trail (1992) have made even further advances, treating exchange exactly, that is, by solving the Schrödinger equation with non-local exchange kernel terms.

### 3 RESULTS AND DISCUSSION

Because the temperature dependence of free–free absorption in the far-IR hinges on low-energy momentum transfer cross-sections, it is appropriate to consider the reliability of current estimates of these data. Results from swarm data below 10 eV are plotted in Fig. 1, the latest observations (England et al. 1988) hardly differ from earlier results (Crompton, Gibson & McIntosh 1969; Gibson 1970; Buckman & Phelps 1985); the only significant departures are from the measurements of Buckman & Phelps above 5 eV.

Crossed-beam cross-sections (Srivastava et al. 1975; Shyn & Sharp 1981; Brunger et al. 1991) are also given in Fig. 1; they are in satisfactory agreement with each other and with the swarm values, that is, well within the predicted errors of about 20 per cent. The consensus is that swarm data provide the most reliable experimental momentum transfer cross-sections.

The latest theoretical estimates based on the SEP method (Morrison et al. 1987); the BFVCC method, treating exchange as a local potential (Buckman et al. 1990; Brunger

![Figure 1. Experimental total momentum transfer cross-sections as a function of E(eV). (Q_m(E) given in units of 10^{-16} cm^2.)](https://academic.oup.com/mnras/article-abstract/269/4/865/982081/10.1093/mnras/269.4.865?redirectedfrom=feed)
et al. 1991; Morrison, private communication); and the same method, treating exchange exactly (Morrison & Trail, private communication; Trail 1992) are given in Fig. 2. It is virtually impossible to distinguish between these theoretical cross-sections graphically; they are also in excellent agreement with England et al.’s (1988) swarm results. Bell et al. (1975) and Bell (1980) did not publish details of their close-coupling momentum transfer cross-sections. The values of $Q_m(E)$ obtained by Hara (1969) are in satisfactory agreement with SEP and BFVCC data, and should correspond closely with Bell et al.’s two-centre computations.

The first computation of $H_2^+$ free–free absorption by Sommerville (1964) used an approximation by Ohmura & Ohmura (1960, 1961), which assumed that s-wave radial orbitals were represented by their asymptotic form, and p-wave orbitals by plane waves. This approximation assumed that s–p transitions were solely responsible for absorption, and coefficients were calculated from the phase shifts of Massey & Ridley (1956). In the far-IR, this method is equivalent to replacing $Q_m(E)$ in equation (2) by its elastic scattering counterpart. John (1975) used the method of Dalgarno & Lane (1966) and the experimental momentum transfer cross-sections of Gibson (1970) and Crompton et al. (1969). These molecular data were considered to be the most accurate available at that time. The two full wavefunction calculations of $H_2^+$ free–free absorption (Bell et al. 1975; Bell 1980), based on the close-coupling method, used a numerical integration to evaluate radiative dipole matrix elements. The first close-coupling computation (Bell et al. 1975) considered only s–p transitions, and the target was restricted to the ground rotational state ($j=0$) and included only spherically symmetric potential terms. The two-centre close-coupling calculation of Bell (1980) allowed for non-spherically symmetric potential components, and evaluated absorption coefficients for s–p and p–d transitions. The p–d terms were found to account for as much as 20 per cent of the total absorption at higher temperatures, not just a few per cent as had been predicted earlier. The consequence of the extra p–d components, and of the addition of excited rotational states and non-spherical potential terms, is to increase absorption coefficients. The differences grow steadily as temperatures are lowered, varying from over 20 per cent at 6300 K to over 30 per cent at 1400 K. The alternative procedure (John 1978) of evaluating matrix elements from analytical functions of the static–exchange phase shifts of Schneider (1975) gave coefficients in reasonable

Figure 2. Total momentum transfer cross-sections from theory and the latest swarm analysis as a function of $E$(eV). $Q_m(E)$ given in units of 10$^{-16}$ cm$^2$. [Theory: —— BFVCC exact exchange, Morrison & Trail (1993, private communication); — BFVCC local exchange, Morrison (private communication), Brunger et al. (1991); × SEP, Morrison et al. (1987); * Two-centre, Hara (1969). Swarm analysis: …… England et al. (1988).]
Figure 3. Scaled $H_2^-$ free–free absorption coefficients in the soft-photon limit, $A(T) = \lim_{\lambda \to \infty} |K^0(T)/\lambda^2|$.

$|K^0(T)|$ given in units of $10^{-26}$ cm$^4$ dyn$^{-1}$, $\lambda$ in $\mu$m. [—— Bell (1980); ——— Bell et al. (1975); • John (1975); × John (1978).]

Table 1. Scaled $H_2^-$ free–free absorption coefficients in the soft-photon limit, $[A(T) = \lim_{\lambda \to \infty} |K^0(T)/\lambda^2|].$

<table>
<thead>
<tr>
<th>T(K)</th>
<th>VCC1</th>
<th>VCC2</th>
<th>VCC3</th>
<th>SEP</th>
<th>Sw1</th>
<th>Sw2</th>
<th>Sw3</th>
<th>2-C</th>
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<tr>
<td>10080</td>
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<td>0.303</td>
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<td>0.384</td>
<td>0.385</td>
<td>0.400</td>
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<td>0.511</td>
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<td>0.528</td>
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<td>0.600</td>
<td>0.593</td>
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<td>0.637</td>
<td>0.641</td>
<td>0.645</td>
<td>0.637</td>
</tr>
</tbody>
</table>

Body frame vibrational close-coupling method: VCC1: exact exchange calculated using elastic momentum transfer data of Morrison & Trail (private communication), Trail (1992); VCC2: exact exchange calculated using the total momentum transfer data of Morrison & Trail (private communication), Trail (1992); VCC3: local exchange calculated using the total momentum transfer data of Morrison (private communication), Morrison & Isaacs (private communication) and Buckman et al. (1990). Static–exchange–polarization method: SEP: calculated using the total momentum transfer data of Morrison et al. (1987).

Two-centre method: 2-C: extrapolated from the results of Bell (1980).

Swarm analysis method: Sw1: calculated using the total momentum transfer data of England et al. (1988); Sw2: calculated using the total momentum transfer data of Buckman & Phelps (1985); Sw3: calculated using the total momentum transfer data of Gibson (1970) and Crompton et al. (1969).
accord with the data of Bell (1980). The closest agreement with Bell's two-centre coefficients was obtained by John (1975), using the method of Dalgarno & Lane (1966); differences were smaller than 2 per cent for temperatures lower than 6300 K. Results for scaled free–free absorption coefficients in the soft-photon limit

\[ \lim_{\lambda \to 0} \left( \frac{K_\lambda(T)}{\lambda^2} \right) \]

are given in Fig. 3.

It is difficult to differentiate graphically between absorption coefficients based on the latest theoretical and swarm data because of the close accord between their momentum transfer cross-sections. Scaled absorption coefficients at zero photon energy are given in Table 1. We find differences of less than 1 per cent between absorption coefficients estimated with the latest swarm data (England et al. 1988) and those estimated with earlier values (Buckman & Phelps 1985; Gibson 1970; Crompton et al. 1969). Coefficients based on theoretical data from SEP and BFVCC methods show similar differences. Free–free absorption computations should be based on the elastic scattering component of momentum transfer. Vibrational excitation is known to make small contributions to cross-sections at low energies; nevertheless, it would be useful to have some measure of this effect on free–free absorption. Data are available for the separate contributions from vibrational transitions 0 → 0, 0 → 1 for the BFVCC method with exact exchange; thus we are able to gauge the errors from using total, as against elastic, momentum transfer cross-sections in this case. We found that absorption coefficients based on total momentum transfer cross-sections were a little larger than those estimated with elastic scattering values; results vary from about 2 per cent at 10 080 K, to 0.9 per cent at 5040 K, to smaller than 0.4 per cent for temperatures lower than 2520 K.

4 CONCLUSIONS

It would appear that free–free absorption coefficients from the SEP method, alternative forms of the BFVCC method, and swarm analysis have converged to a common set of values. The quality of agreement between the basic molecular data, and the effect of thermal averaging smoothing out any dissimilarities, supports the case that changes greater than about 2 per cent are unlikely. The most accurate values of H\(_2^+\) free–free absorption currently available are given by the exact exchange version of the BFVCC method based on elastic momentum transfer cross-sections.

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REFERENCES

Lane N. L., 1980, Rev. Mod. Phys., 52, 29
Massey H. S. W., 1976, Negative Ions, 3rd edn. Cambridge Univ. Press, Cambridge