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LETTER TO THE EDITOR

Electron collisions with ClO using the R-matrix method

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Abstract. The R-matrix method is used to calculate elastic and the excitation cross sections of the six lowest lying electronically excited states of the ClO molecule. These states, of symmetry $1\,^4\Sigma^-$, $A\,^2\Pi$, $1\,^2\Sigma^-$, $1\,^2\Delta$, $2\,^4\Sigma^-$ and $1\,^2\Sigma^+$, have vertical excitation energies in the range 3.48 to 6.99 eV. Except for the state $A\,^2\Pi$, all other excited states are dissociative. We find a bound state of ClO^- with $^1\Sigma^+$ symmetry with an adiabatic electron affinity of 1.128 eV at an equilibrium bond length of 3.25 a_0. There are shape resonances of $^1\Pi$ and $^3\Pi$ symmetries at 1.6 and 2.9 eV respectively. Rotationally summed cross sections are obtained for elastic and electronically inelastic scattering for electron-impact energies up to 10 eV.

1. Introduction

Chlorine-containing molecules play a particularly important role in the removal of ozone and atomic oxygen in the Earth's upper atmosphere and are therefore important in global stratospheric ozone loss. We wish to study electron collisions with chlorine oxides to aid ongoing atmospheric studies. Experimental work on Cl_xO_y systems is difficult because these molecules, which are highly reactive and unstable, have to be chemically produced *in situ*. Experimental work on electron collisions with ClO_2 and Cl_2O has only recently been reported (Davis *et al* 1995, Gulley *et al* 1998, Marston *et al* 1998, Motte-Tollet *et al* 1997, 1998). Studies of other Cl_xO_y systems are underway. It is therefore necessary to perform theoretical studies for comparison with these experiments and to provide insight into the scattering mechanisms from such targets.

The open shell nature of many of the Cl_xO_y compounds makes them difficult systems to treat theoretically. Electron correlation plays an important role in these systems, not only for characterizing the ground state wavefunction, but also in the excitation of the many low lying excited states which significantly affect low energy electron collisions.

In this letter we report the first electron collision calculations on ClO. These calculations are performed using the UK polyatomic R-matrix code (Morgan *et al* 1997, 1998) taking particular advantage of the ability of this method to provide a good representation of the electron correlation in several excited states of the molecule (Tennyson 1996a).

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2. Method

2.1. General considerations

The R-matrix method (Burke and Berrington 1993) divides configuration space into two regions. In the inner region, here defined by a sphere of radius 10 a_0 centred at the ClO centre of mass, the wavefunction is written using the configuration interaction (CI) expression:

$$\Psi_k = \mathcal{A} \sum_{ij} a_{ijk} \phi_i^N \eta_{ij} + \sum_j b_{jk} \phi_j^{N+1} \tag{1}$$

where ϕ_i^N represents the ith state of the N-electron target, η_{ij} is a function representing the continuum electron and $\mathcal{A}$ an anti-symmetrization operator. The continuum functions are the only functions with amplitude on the R-matrix boundary. The second sum in (1) comprises configurations composed of short-range functions. To obtain reliable results it is important to maintain a balance between the N-electron target representation, ϕ_i^N, and the $N + 1$-electron scattering wavefunction, Ψ_k. The choice of appropriate ϕ_j^{N+1} is crucial in this (Tennyson 1996b). Coefficients a_{ijk} and b_{jk} are variational parameters determined as a result of the matrix diagonalization.

Inside the R-matrix sphere full electron–electron and exchange interactions are explicitly modelled. Outside the sphere, only long-range multipolar interactions between the scattering electron and the various target states are included. ClO is a strongly dipolar system which has a dipole moment of 1.23 D (Pettersson *et al* 1986). This has to be taken into account both by propagating the R-matrix to a large distance, 50 a_0 in the present work, and by considering convergence with respect to the partial wave expansion used for the continuum orbitals, η_{ij}.

2.2. Target states

There are a number of older *ab initio* electronic structure calculations on ClO available in the literature (Arnold *et al* 1977, Petterson *et al* 1986). Recently, new calculations have become available, (Lane *et al* 1999, Toniolo *et al* 2000, Lane and Orr-Ewing 2000) inspired, at least in part, by new laser cavity ring down laser experiments (Howie *et al* 1999).

Our calculations on ClO used the double zeta plus polarization Gaussian basis set of Dunning and Hay (1977), and Magnusson and Schaefer (1985). ClO is a linear molecule with a $^2\Pi$ symmetry ground state. The highest symmetry group available for ClO in our polyatomic R-matrix code is C_{2v}. In this symmetry the partly occupied 3π orbital has a b_1 and a b_2 component, see table 1. These orbitals are split by a self consistent field (SCF) calculation on the ground state. To avoid splitting the symmetry, two SCF calculations were performed with $^2B_1$ and $^2B_2$ symmetry. The a_1 and a_2 orbitals, and the total energy, obtained from these calculations are identical but the b_1 and b_2 orbitals are not. Our CI calculations used b_1 orbitals from the $^2B_2$ symmetry SCF calculation and b_2 orbitals from the $^2B_1$ calculation.

A number of CI models were considered, mostly of the complete active space (CAS) valence CI variety. The largest model tested was one in which the Cl 1s, 2s and 2p electrons, along with O 1s electrons, were frozen in their SCF orbitals. These orbitals are all bound by at least 220 eV. The remaining electrons were allowed to move freely between the Cl 3s and 3p, and O 2s and 2p orbitals, whose SCF binding energies were all less than 40 eV. This CAS type wavefunction can be written $(1\sigma, 2\sigma.3\sigma, 4\sigma, 1\pi)^{12}(5\sigma, 6\sigma, 7\sigma, 8\sigma, 2\pi, 3\pi, 4\pi)^{13}$. However, it was found that target excitation energies and dipoles were largely unaffected if the 5σ and 6σ orbitals bound by 38 eV and 28 eV respectively, were also frozen. The new model, which only considered active electrons in orbitals bound by less than 20 eV, was thus $(1\sigma, 2\sigma, 3\sigma, 4\sigma, 5\sigma, 6\sigma, 1\pi)^{16}(7\sigma, 8\sigma, 2\pi, 3\pi, 4\pi)^9$. This model was compared with the much

Table 1. Vertical energy excitations (in eV) for the ClO target states generated using a $(7\sigma, 8\sigma, 2\pi, 3\pi, 4\pi)^9$ CAS CI model at bond length 3.15 a_0. Also given are the dominant configuration of each state, the number of configurations, N, in the CAS and the excitation values of Toniolo *et al* (2000).

			Vertical excitation energy	
State	Configuration	N	This work	Toniolo *et al*
$X\ ^2\Pi$	$7\sigma^2 2\pi^4 3\pi^3$	602	0	0
$1\ ^4\Sigma^-$	$7\sigma^2 2\pi^4 3\pi^2 8\sigma^1$	352	3.48	3.69
$A\ ^2\Pi$	$7\sigma^2 2\pi^3 3\pi^4$	602	4.82	4.82
$1\ ^2\Sigma^-$	$7\sigma^2 2\pi^4 3\pi^2 8\sigma^1$	568	4.98	
$1\ ^2\Delta$	$7\sigma^2 2\pi^4 3\pi^2 8\sigma^1$	568	5.17	
$2\ ^4\Sigma^-$	$7\sigma^2 2\pi^3 3\pi^3 8\sigma^1$	352	6.52	
$1\ ^2\Sigma^+$	$7\sigma^2 2\pi^4 3\pi^2 8\sigma^1$	568	6.99	

higher level *ab initio* calculations available (Toniolo *et al* 2000) and the results were found to be in surprisingly good agreement.

Table 1 compares vertical excitation energies for the states considered in our calculation. Although the present study is primarily concerned with the ClO equilibrium geometry, a comparison of potential energy curves computed with our present model with those of Toniolo *et al* (2000) also gave excellent agreement, with our calculations even reproducing the avoided crossing involving the $A\ ^2\Pi$ state at $R \sim 4.1\ a_0$. Our calculation gives a ClO equilibrium geometry of $R_e = 3.15\ a_0$, close to the most recent value of $R_e = 3.03\ a_0$ (Toniolo *et al* 2000). Except where stated otherwise, all results presented here are for the nine electron CAS model at $R = 3.15\ a_0$.

Our model gives a ClO equilibrium dipole moment of 1.21 D, close to the value of 1.23 D calculated by Pettersson *et al* (1986) using a sophisticated multi-reference CI method.

2.3. Scattering model

Our final calculations used the seven target states given in table 1 in the close-coupling expansion, see equation (1), although a variety of test calculations were performed with fewer states in this expansion. Calculations were performed for singlet and triplet states with A_1, B_1, B_2 and A_2 symmetries. In all calculations, the continuum orbitals were represented by Gaussians centred at the molecule centre of gravity. For this, the orbitals of Sarpal (1991) were used. Most test calculations were performed for continuum orbitals up to f ($l \leqslant 3$), our final calculations included g orbitals in all the calculations. These continuum orbitals were orthogonalized to the target orbitals retained in the calculation and those with an overlap of less than 2×10^{-7} were removed (Morgan *et al* 1997).

Test calculations, from static exchange upwards, were performed to test the stability of our model and assign resonances. These calculations included some with hand picked configurations which allowed us to give orbital designations to the resonances we found and to probe the cause of pseudo-resonances which are high energy artifacts of any truncated coupled channels calculation.

One advantage of the CAS CI target model employed here is that the ϕ_j^{N+1} functions in equation (1) can be defined in a fashion which retains the balance of the calculation (Tennyson 1996b). All $N + 1$-electron configurations of the appropriate total symmetry given by $(1\sigma, 2\sigma, 3\sigma, 4\sigma, 5\sigma, 6\sigma, 1\pi)^{16}(7\sigma, 8\sigma, 2\pi, 3\pi, 4\pi)^{10}$ were retained. Furthermore, the 9σ and 5π orbitals were retained in the calculation to allow for short-range correlation effects. The

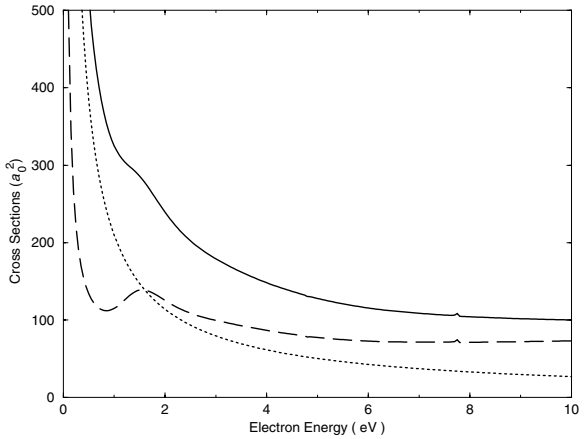

Figure 1. Rotationally summed elastic cross sections for electron impact on ClO ($X\ ^2\Pi$): Long-dashed curve, R-matrix elastic cross sections up to $l = 4$; dotted curve, Born correction; solid curve, final.

lowest target a_2 orbital, which is a δ orbital was also retained. These orbitals were treated in the same fashion as the continuum orbitals, η_{ij}, in equation (1) (Tennyson 1996b). In practice the calculations showed little sensitivity to whether these correlation orbitals were retained or not.

3. Results

3.1. Bound state: ClO^-

The dipole moment of ClO is sufficiently strong to support a bound state of the anion. All our models (except static exchange) found a bound state of ClO^- with $^1\Sigma^+$ symmetry. The energy of state was determined using our bound state detecting code BOUND (Sarpal *et al* 1991, Morgan *et al* 1998). Our model gave ClO an electron affinity of 1.087 eV at $R = 3.15\ a_0$.

As a check on this finding we performed a standard bound state quantum chemistry calculation on ClO^- using the same orbitals and a model employed for the scattering calculations. This calculation gave a very similar result, a ClO electron affinity of 1.098 eV at $R = 3.15\ a_0$. Scattering calculations of $^1A_1$ symmetry were repeated as a function of internuclear separation, R, to determine the characteristics of the $X\ ^1\Sigma^+$ state of ClO^-. Our calculations gave an equilibrium bond length of ClO^- of 3.25 a_0, somewhat longer than that of ClO, and an adiabatic electron affinity of 1.128 eV.

At large R, our calculations predict that the electron affinity of ClO goes to zero. This is clearly incorrect as both Cl and O form stable negative ions. However, our continuum basis set, which provides the diffuse orbitals necessary for binding the anionic electron, are located at the centre of the molecules. At large R, this electron is associated with only one of the atoms. Under these circumstances, the location of the diffuse orbitals is no longer appropriate.

3.2. Elastic scattering

The elastic scattering cross section is formally divergent in the fixed-nuclei approximation, due to the presence of a permanent dipole. However, in the adiabatic-nuclei approximation the partial elastic cross sections can be exploited to yield rotational cross sections summed over all final rotor state quantum numbers, which are independent of the initial rotor state (Norcross

and Padial 1982). It is well known that the cross sections of dipole dominated processes only converge slowly with partial waves. States with $l > 4$ omitted from our calculations were allowed for using the Born approximation (Chu and Dalgarno 1974). In figure 1, we present rotationally summed cross sections summed over all symmetries. The rotational constant of ClO at the equilibrium geometry was taken as 0.6205 cm^{-1}.

For all models, our results are characterized by a sharp rise, proportional to E^{-1}, in the elastic scattering cross section at energies below 1 eV for each symmetry. This behaviour has been noted previously for strongly dipolar molecules (Fabrikant 1977). Indeed, test calculations which set the ClO ground state dipole moment to zero in the outer region led to the disappearance of this threshold feature.

All calculations showed resonance features in the cross section near 2 eV. Analysis of the eigenphase sums showed these to be resonances of both $^1\Pi$ and $^3\Pi$ symmetries and to correspond to shape resonances with the same configuration $3\pi^3 8\sigma^1$. These resonances lie close to each other in all models although they move to lower energy and become narrower as the number of states in the calculation is increased. In our final model with seven states, the position and width of the resonance with $^3\Pi$ symmetry are 1.589 eV and 0.664 eV, respectively, and the corresponding quantities for $^1\Pi$ symmetry are 2.915 eV and 1.199 eV. Besides the resonances, careful analysis of these cross sections shows small structures at some of the thresholds in the calculation. There is also a small bump at 7.8 eV. This energy is close to that of a $^4\Pi$ state which is the lowest lying target state omitted from our calculation. This feature, and the more prominent ones at the same energy apparent in some of our inelastic cross sections, are probably therefore an artefact of an incomplete calculation.

The present calculations have also located two Π Feshbach resonances. The triplet Feshbach resonance which can be seen as a broad feature in figure 2(*b*) is located at 6.303 eV with a width of 0.543 eV. The singlet Feshbach resonance, prominent in figure 2(*d*), is much narrower; it is located at 5.527 eV with a width of 0.102 eV. There is also a pseudo-resonance around 8.7 eV, shown in figure 2(*d*). Both Feshbach resonances have configuration $2\pi^3 3\pi^4 8\sigma$. These resonances are present only when the $2\,^4\Sigma^-$ state is included in the calculation and hence this state must be considered their parent.

3.3. Inelastic cross sections

With the exception of the A $^2\Pi$ state, all the electronically excited states of ClO considered in this calculation are dissociative, and even for the A $^2\Pi$ state many levels are rapidly dissociated by crossings (Howie *et al* 1999), of which there are many (Lane *et al* 1999). Thus, although we discuss our results below in terms of electron-impact electronic excitation, it should be borne in mind that essentially all excitations will lead to dissociated Cl and O.

Figure 2 presents electron-impact electronic excitation cross sections from the ground state to the various excited states included in the calculations. The contribution of angular momentum states higher than $l = 4$ for dipole allowed transitions to states A $^2\Pi$, 1 $^2\Sigma^-$, 1 $^2\Delta$ and 1 $^2\Sigma^+$ is included via the Born approximation (Chu and Dalgarno 1974). The dipole transition moments (in au) of these states from the ground state are 0.2623, −0.0456, 0.0458 and 0.1126 respectively. The Born correction is higher for transitions having higher transition moment and higher excitation threshold. Except for the transition X $^2\Pi$–A $^2\Pi$, the Born correction for other electronic transitions from the ground state is negligible, in most cases it cannot be seen on the scale of the figure. This is due to their small transition moments.

Of all the six excitation transitions from the ground state, the cross section for the transition X $^2\Pi$–A $^2\Pi$ is largest. The state A $^2\Pi$ lies closest to the ground state and is of the same symmetry, this transition is also optically strong (Howie *et al* 1999). This excitation may be

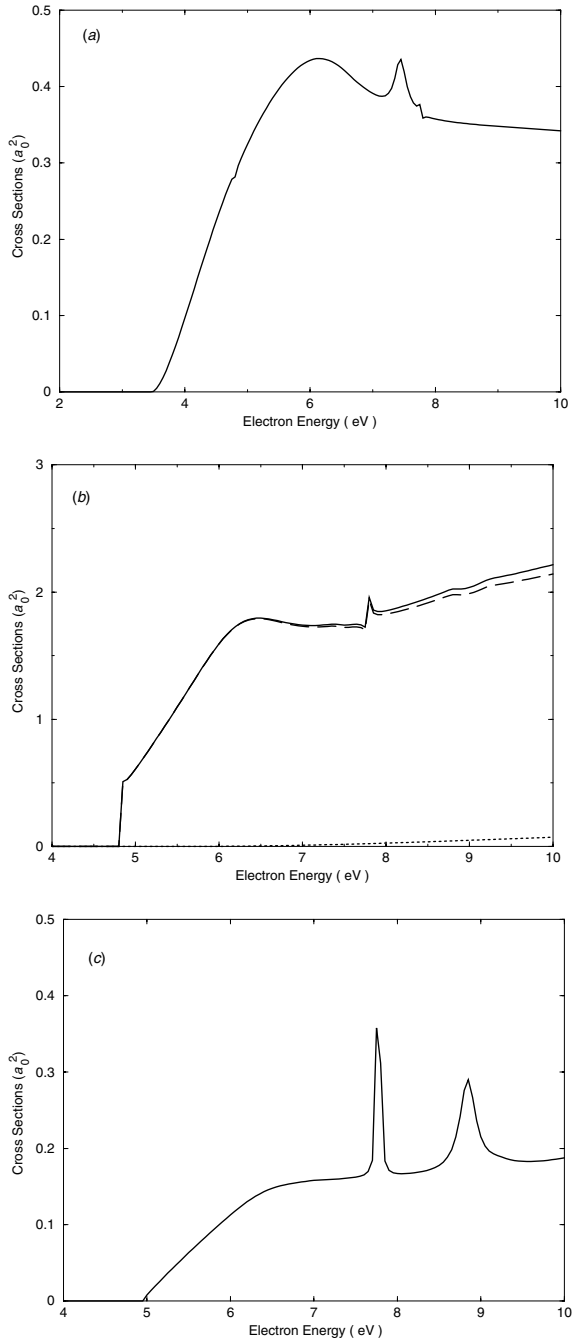

Figure 2. Electron-impact electronic excitation of cross sections for ClO. Long-dashed curve, R-matrix cross sections up to $l = 4$; dotted curve, Born correction; solid curve, final cross section. For figure 2(d) only, the contribution due to the $^3B_1$ symmetry and the other symmetries are also shown separately as thin curves. (a) X $^2\Pi$–1 $^4\Sigma^-$; (b) X $^2\Pi$–A $^2\Pi$; (c) X $^2\Pi$–1 $^2\Sigma^-$; (d) X $^2\Pi$–1 $^2\Delta$; (e) X $^2\Pi$–2 $^4\Sigma^-$; (f) X $^2\Pi$–1 $^2\Sigma^+$.

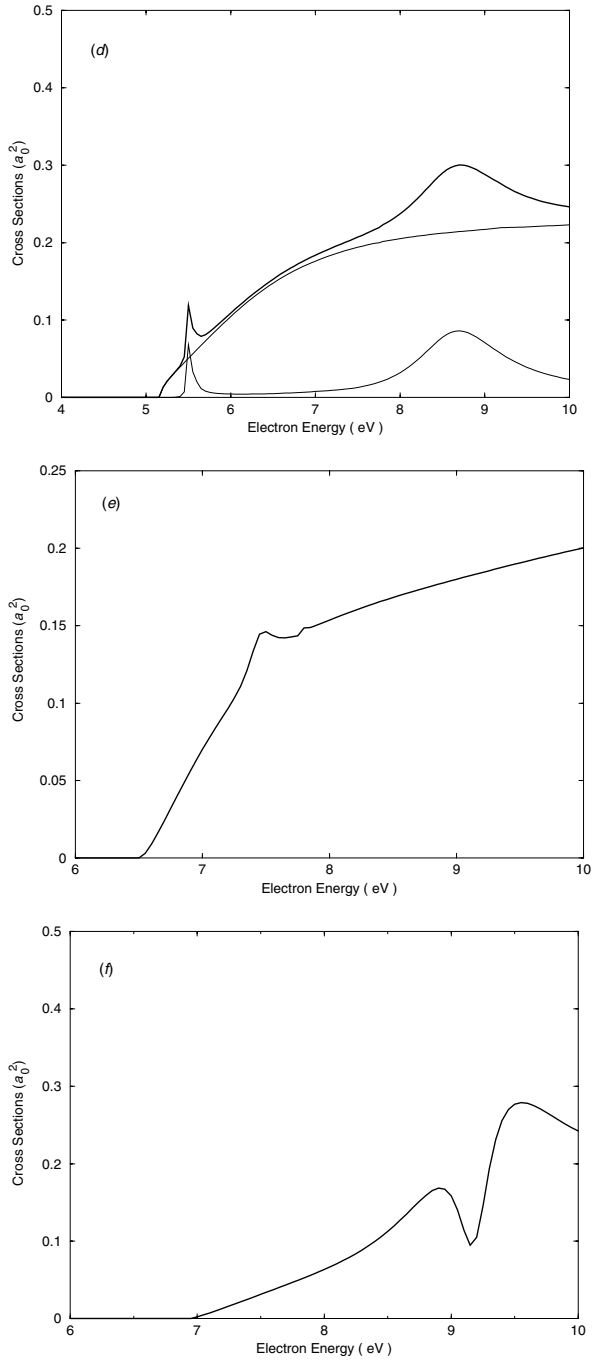

Figure 2. Contiuned.

responsible for the catalytic reduction of stratospheric ozone due to dissociation of the $A\,^2\Pi$ state into its atomic products.

4. Conclusions

This is the first study of electron impact on open-shell radical ClO. It provides a number of suggestions as to what might be observed in any experimental investigation. These include the presence of low lying shape resonances and a higher lying Feshbach resonance and detection of a ClO^- anion. Models developed in this paper are currently being applied to electron collisions with polyatomic Cl_xO_y molecules, in particular OClO and Cl_2O.

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References

Arnold J O, Whiting E E and Langhoff S R 1977 *J. Chem. Phys* **66** 4459–67
Burke P G and Berrington K A (ed) 1993 *Atomic and Molecular Processes: an R-Matrix Approach* 1993 (Bristol: Institute of Physics Publishing)
Chu S I and Dalgarno A 1974 *Phys. Rev.* A **10** 788–92
Davis J A, Mason N J, Marston G and Wayne R P 1995 *J. Phys. B: At. Mol. Opt. Phys.* **28** 4179–87
Dunning T H and Hay P J 1977 *Methods of Electronic Structure Theory* vol 2 ed H F Schaefer (New York: Plenum)
Fabrikant I I 1977 *J. Phys. B: At. Mol. Phys.* **10** 1761–8
Howie W H, Lane I C, Newman S M, Johnson D A and Orr-Ewing A J 1999 *Phys. Chem. Chem. Phys.* **1** 3079–85
Gulley R J, Field T A, Steer W A, Mason N J, Lunt S L, Ziesel J P and Field D 1998 *J. Phys. B: At. Mol. Opt. Phys.* **31** 5197–208
Lane I C, Howie W H and Orr-Ewing A J 1999 *Phys. Chem. Chem. Phys.* **1** 3087–96
Lane I C and Orr-Ewing A J 2000 *Mol. Phys.* **98** 793–806
Magnusson E and Schaefer H F 1985 *J. Chem. Phys.* **83** 5721–6
Marston G M, Walker I C, Mason N J, Gingell J M, Zhao H, Brown K L, Motte-Tollet F, Delwiche J and Siggel M R F 1998 *J. Phys. B: At. Mol. Opt. Phys.* **31** 3387–405
Morgan L A, Gillan C J, Tennyson J and Chen X 1997 *J. Phys. B: At. Mol. Opt. Phys.* **30** 4087–96
Morgan L A, Tennyson J and Gillan C J 1998 *Comput. Phys. Commun.* **114** 120–8
Motte-Tollet F, Delwiche H, Hubin-Franskin M J, Gingell J M, Jones N C, Mason N J and Marston G 1998 *Chem. Phys. Lett.* **284** 452–8
Motte-Tollet F, Ska M P, Marston G M, Walker I C, Siggel M R F, Gingell J M, Kaminski L, Brown K L and Mason N J 1997 *Chem. Phys. Lett.* **275** 298
Norcross D W and Padial N T 1982 *Phys. Rev.* A **25** 226–38
Pettersson L G M, Langhoff S R and Chong D P 1986 *J. Chem.Phys* **85** 2836–44
Sarpal B K 1991 Private communication
Sarpal B K, Branchett S E, Tennyson J and Morgan L A 1991 *J. Phys. B: At. Mol. Opt. Phys.* **24** 3685–99
Tennyson J 1996a *J. Phys. B: At. Mol. Opt. Phys.* **29** 1817–28
——1996b *J. Phys. B: At. Mol. Opt. Phys.* **29** 6185–201
Toniolo A, Persico M and Pitea D 2000 *J. Chem. Phys.* **112** 2790–7