Mössbauer Studies on some Europium(III) β-Diketonate Complexes

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Some Europium(III) dibenzoylmethide and benzoylacetonate complexes have been subjected to Mössbauer studies at liquid nitrogen temperature. An attempt is made to discuss covalency in these complexes in terms of 6s, 4f and/or 5d orbital participation in the bond formation. Small linewidths are correlated to less symmetric structures. Resonance effects reflect the polymeric nature of these chelates.

Introduction

The generally held theory of bonding in rare-earth compounds is that they are predominantly ionic and that the 4f electrons can not take part in bonding owing to the fact that they are effectively shielded from interaction with external forces by the outer 5s and 5p orbitals [1, 2]. These orbitals are unavailable spatially, not energetically, as they simply do not extend out far enough to join in bonding to any appreciable extent [3]. The above theory of bonding was challenged in recent years. A considerable amount of covalency has been detected in lanthanide compounds [4–18]. The study on lanthanide shift reagents indicates a large contact contribution to the chemical shifts [6–9], especially for ^{13}C resonances [10]. The possibility of f-orbital participation in covalent bond formation in lanthanide and actinide complexes has been mentioned since years [11–18].

Earlier Mössbauer studies on europium complexes [19–33] suggest that the compounds are predominantly ionic with little contribution from covalency. Some workers have suggested that the possible mechanism by which the covalent bonding in the compounds arises could be through the participation of 4f orbitals of europium [21, 23, 25]. Other reports suggest that the isomer shift of most of the Eu(III) complexes could be explained on the basis of non-zero density of 6s electrons at the Eu nucleus and the partial covalent bond involving the participation of 5d and 6s orbitals [29, 31]. Recent work of Cashion et al. [34, 35] implies both 6s and 4f participation in bonding. In this paper we attempt to further discuss this problem in the light of recent data on bonding and f-orbital participation in lanthanide compounds.

Moreover, it is well known that β-diketonate complexes tend to get polymerized if the coordination number is not satisfied with the monomer and if the ligands sterically allow such polymerization [36–38]. Mössbauer resonance effect studies can be used to study such type of intermolecular forces [27, 28].

Experimental

a) Preparation of the Complexes

The complexes given in Table 1 have been prepared by standard methods given in the literature [39–42]. All the reagents used were either chemically pure or analar grade. The purity of the samples was determined by chemical analyses.

b) Mössbauer Studies

The details of the Mössbauer spectrometer have been discussed elsewhere [43]. An ND 512 multichannel analyzer was used in the multiscaling mode

Table 1. Mössbauer data of the Eu(III) complexes.

Complexes	Isomer shift* (mm/s)	Line-width (mm/s)	Resonance effect
$Eu(DBM)_3$	0.68 ± 0.02	2.82 ± 0.02	18.52
$Eu(DBM)_3 \cdot H_2O$	0.66 ± 0.02	2.55 ± 0.03	11.03
$NaEu(DBM)_4$	0.65 ± 0.02	2.83 ± 0.10	11.06
$Eu(DBM)_2Ac$	0.68 ± 0.04	3.16 ± 0.04	28.24
$Eu(DBM)_2Bz$	0.61 ± 0.02	2.65 ± 0.03	21.80
$Eu(DBM)_2(p\text{-}NO_2Bz)$	0.61 ± 0.05	3.44 ± 0.04	24.69
$Eu(BA)_3 \cdot 2\,H_2O$	0.59 ± 0.03	2.82 ± 0.18	17.95
$NaEu(BA)_4$	0.73 ± 0.02	2.36 ± 0.03	17.55
$Eu(BA)_2Ac$	0.66 ± 0.04	2.66 ± 0.04	30.24
$Eu(BA)_2(oxine)$	0.72 ± 0.03	2.70 ± 0.03	8.42

DBM = dibenzoylmethide; BA = benzoylacetonate; Ac = acetate, Bz = benzoate, p-NO_2Bz = para-nitrobenzoate; oxine = 8-hydroxyquinolinate.

* w.r.t. EuF_3 as standard reference.

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for data acquisition. The spectrometer was operated in the sinusoidal velocity mode. The folding point was determined accurately to a fraction of a channel corresponding to the maximum velocity. The zero of the spectrometer was obtained with the help of the accurately measured drive-frequency, and the memory advance frequency. In the spectrometer used by us, both these frequencies were derived from the same crystal oscillator. Thus, the zero of the spectrometer was fixed without any external calibration standards. In all our measurements the zero of the spectrometer was also checked independently with standard absorbers. Standard spectra of enriched iron were obtained both before and after the spectrum of each europium compound was taken.

A 10 mc Sm-151 source in the form of samarium oxide procured from Harwell was used for all measurements. The 21.6 keV γ-rays of Eu-151 were detected in a 2 mm thick NaI(Tl) crystal coupled to a RCA 6342 photomultiplier and an ORTEC Model 410 linear amplifier. The resonance effect (area under the resonance curve) observed for the europium oxide absorber was approximately 40%. Accurately weighed absorbers were sandwitched between two cellulose tapes and were fixed in a standard geometry in a lead block. The errors were obtained from the uncertainty in locating the peak positions. In general, we have given high estimates of the errors.

The names of the complexes, linewidths, resonance effects and the isomer shifts are given in Table 1.

Results and Discussion

(i) Isomer Shifts (IS)

The IS reported in Table 1 are relative to EuF_3. Of the europium complexes studied here only the room temperature spectrum of $NaEu(BA)_4$ has been reported previously. All the IS are positive w.r.t. EuF_3 and fall in the range 0.59–0.73 mm/s.

Since a considerable amount of confusion exists in the literature regarding the interpretation of the IS data and metal-ligand covalency in europium complexes, we discuss this in some detail.

For the purpose of comparison, the IS can be expressed as

$$\delta \propto (\partial R/R)[|\Psi(0)|_a^2 - |\Psi(0)|_s^2],$$

where R is the radius of the nucleus in the ground state, δR is the difference between the radii of the excited state and the ground state and $|\Psi(0)|_a^2$ and $|\Psi(0)|_s^2$ indicate the electron densities at the absorber and source (or standard reference substance) nuclei, respectively. Since the δR term is positive for ^{151}Eu, an increase in IS will indicate an increase in $|\Psi(0)|_a^2$ relative to the source (or reference). This change in electron density at the nuclei depends on two factors: (a) increasing participation of the 6s orbital and (b) shielding by the electrons in the f, p or d orbitals. Since Eu^{3+} is a "hard" cation (or class A acid) one would expect that the dominant contribution to covalency is through a ligand to metal donation of electrons. Hence the sign and magnitude of IS will be the resultant of the above two contributions.

It has been pointed out in the literature [34] that rare-earth trifluorides represent a very good approximation to ionic salts for IS purposes. Therefore the Eu^{3+} ion in EuF_3 can be assumed to be free of all covalency effects and corresponds to an electronic configuration $4f^6\,6s^0$. Considering the effect of covalency, the following electronic configuration had been assumed in the literature for Eu^{3+} ion in europium complexes:

(a) $4f^6\,6s^x$ [29, 31],
(b) $4f^{6+y}\,6s^0$ [21, 23],

where x and y are the amounts of electron density donated by the ligands to the s and f orbitals, respectively.

Addition of electrons to a 6s orbital will increase the s-electron density at the nucleus and make IS more positive w.r.t. a given standard. On the basis of Mössbauer studies on europium metal [19, 44, 45] one can estimate the contribution of one s-electron to the IS in europium compounds. It can be shown [31] that the addition of one s-electron ($x = 1$) to the purely ionic Eu^{3+} is to *increase* the IS by +9 mm/s. Similarly, the effect of addition of one f-electrons ($y = 1$) to purely ionic Eu^{3+} is to *decrease* the IS by −13.5 mm/s. Hence the IS measurements are not equally sensitive to the two types of bonding — the effect of 4f electrons on the IS is approximately double and opposite in sign to that of 6s electrons. It has been shown [46] that the effect of 5d electrons is about five times smaller and opposite in sign to that of a 6s electron. Covalency with 6p electrons is also possible but difficult to detect from IS measurements [34].

An alternative interpretation of Mössbauer results will be to include both (a) 6s and (b) 4f, 5d orbital participation. Here we assume an electronic configuration for the Eu^{3+} ion in europium chelates as

$$4f^{6+y}\,6s^{x}\,.$$

We consider σ-bonding with 6s orbitals and π-bonding with 4f or 5d orbitals of europium with ligand orbitals of appropriate symmetry. A metal-ligand σ-bond will increase the s-electron density at the europium nucleus due to ligand → metal charge transfer. An increase in IS due to this effect may be compensated to some extent by a small 4f or a large 5d orbital participation. In fact 5d-electrons can dominate the bonding [34] but not the IS.

The net effect is that inspite of a large covalency the IS will be very near the purely ionic compounds. The situation can be best illustrated by using EuBr$_3$ as an example. If one assumes covalency only due to 6s participation then one finds $x \approx 0.018$ from the IS of 0.166 mm/s [47]. It follows, therefore, that EuBr$_3$ is a highly ionic compound. Recently reports on the bonding of rare earth trihalides [4, 5] contradict this fact. A considerable amount of literature exists on the covalent bonding in lanthanide chelates [4—18].

The small IS in Table 1 and in other complexes can be explained if one assumes an electronic configuration of europium in these compounds as $4f^{6+y}\,6s^{x}$. For small +ve IS $x \gg y$, implying a strong σ-bond and a weak π-bond. A large value of x corresponding to large 6s participation will make the IS large and +ve. If one now considers the donation of P_{π}-electrons of bromide (in EuBr$_3$) to the 4f orbital of europium the IS will be small and positive for a large value of x relative to y. Thus it can be inferred from above that the small positive IS need not necessarily be due only to small 6s orbital participation. There may be a small 4f participation (or a large 5d participation) but still the IS can be small and positive w.r.t. EuF$_3$ due to a larger amount of electron density transferred to the 6s orbital.

The following are the general patterns one can see from the data in Table 1. The DBM and BA complexes studied in this work show a much larger IS than the AcAc complexes reported on in the literature [28, 31, 32]. Assuming the f-orbital involvement to be small *relative* to 6s orbital participation one finds a stronger Eu–O covalent bond in the DBM chelates. A satisfactory explanation for this is the resonance and inductive effect of the substituent groups. When $R_1 = R_2 = C_6H_5$ in Fig. 1 the benzene ring is in conjugation with the carbonyl–Eu bond. This facilitates, most effectively at low temperatures, a strong ligand-metal covalency through electron donation to metal orbitals. This is particularly interesting, because it has been reported in the literature that the fluorescence intensity of Eu chelates is dependent on Eu–O covalency [48, 49].

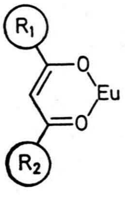

Fig. 1.

Fluorescence data of Fillipescu et al. [50] on Eu and terbium β-diketonates clearly show that "atomatic" β-diketonates (DBM, BA) have higher relative fluorescence intensity than "aliphatic" ones (AcAc). But closer analyses of the IS data in Table 1 and in the literature [32] show that there is no meaningful relationship between the IS data and the fluorescence intensity in most other chelates. A possible explanation for this may be that IS depends, apart from covalency, on many other factors like the second order doppler shift, coordination number and unresolved quadrupole interactions [51] in the Eu Mössbauer spectrum. Therefore it is not possible to analyze covalency in detail. Moreover, because of the complex nature of orbital participation it is not possible to estimate the degree of covalency in these complexes.

(ii) Linewidth

The 21.64 keV resonance is a nuclear 7/2 → 5/2 magnetic dipole transition which should show an eight line quadrupole splitting in compounds with low crystallographic symmetry. The full width at half maximum (FWHM) for these compounds is in the range 2.36—3.44 mm/s which is much larger than the natural width of 1.33 mm/s. Even though the individual lines are not resolved, the overall width of the spectral envelope can give a measure of the quadrupole splitting present. Dulaney and

Clifford [47] have investigated a number of europium oxide systems and found that the symmetric compounds exhibit greatest line broadening. For example, cubic Eu_2O_3 has a larger linewidth (3.40 ± 0.08 mm/s) as compared to anhydrous $EuCl_3$ (2.39 ± 0.02 mm/s). A qualitative explanation given for this was the distortion of f-electron distribution by the surrounding ligands in a highly symmetrical crystal.

Since the crystal structure of none of these chelates is known it is difficult to interpret the linewidths without possible error. The structure of $[Eu(DBM)_4]^-$ ion was described as a square antiprism [52], and $[Eu(BA)_4]^-$ can be considered to be a distorted square antiprism similar to $[Eu(BA)_4]$ [Pip] [53–55]. $Eu(DBM)_3 \cdot H_2O$ can be considered to have a structure which is seven coordinated distorted capped trigonal prism similar to $Yb(acac)_3 \cdot H_2O$ [56]. Similarly $Eu(DBM)_3$ and $Eu(\beta\text{-dk})_2X$ chelates are assumed to have a polymeric structure similar to $Eu(acac)_3$ and $Eu(acac)_3 \cdot OH$ [31]. $Eu(BA)_3 \cdot 2\,H_2O$ is probably a distorted square antiprism similar to $Eu(TTA)_3 \cdot 2\,H_2O$ [57].

From Table 1 it can be seen that $Eu(DBM)_3$ and $NaEu(DBM)_4$ have larger linewidths than the less symmetric (C_{2v}) $Eu(DBM)_3 \cdot H_2O$. The linewidths of all the chelates of the type $Eu(\beta\text{-dk})_2X$ are more than twice the natural linewidth, indicating that these compounds are polymeric six coordinated rather than five coordinated monomers [41]. An interesting feature of these results is that the BA complexes, $Eu(BA)_2Ac$ and $NaEu(BA)_4$ show very small width as compared to their corresponding DBM analogues. The low symmetry of the BA complexes is probably due to the unsymmetrical substitution in the β-diketonate ring. It is known that different radicals attached to the chelate ring effect both the metal-oxygen distance and the electron density associated with the oxygen atoms bound to the ion [50].

(iii) Resonance Effect

The resonance effect in the complexes were calculated from the area under the resonance absorption curve which has been shown to be preferable to the method in which the effect is calculated by computing the percentage decrease in count-rate [58]. The resonance effect is a measure of the forces which hold the europium atoms together in a solid. It has been established that monomers have a low resonance effect whereas polymeric complexes have much larger resonance absorption [27, 28].

The resonance effect of the chelates of the type $Eu(\beta\text{-dk})_2X$ are surprisingly large indicating a polymeric nature of these chelates. If one considers monodentate carboxylate binding then the lone pair of electrons from the carbonyl oxygen can be donated to occupy the sixth coordination position of another molecule. The resultant polymeric chain is shown in Figure 2:

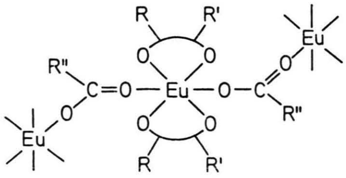

Fig. 2.

The resonance effect in other molecules corresponds to the expected structures. No doubt there seems to be a correlation between resonance effect and polymeric nature in chelates, but additional structural work has to be done to establish the validity of the Mössbauer assignments and the nature of the intermolecular forces.

A very interesting point to note is that the effects observed at room temperature are very small (< 1%) for all these chelates. At liquid nitrogen temperature a dramatic increase in the resonance absorption is seen. A similar observation is also reported in the literature [29] for DBM and BA chelates. The reason for this is not clear. The fluorescent intensity of some of these chelates shows similar trends at room and liquid nitrogen temperature [39, 50, 60, 61]. Since the efficiency of the radiationless intramolecular energy transfer is related to the Eu–O covalent bond [48, 49], the above fact is probably related to intramolecular bonding.

Conclusion

Even though the covalency in europium(III) complexes can be explained through 6s orbital participation, there is fairly good indication of some 4f character in the covalency as the Eu ion tries to attain half filled $4f^7$ shell. Although it is not possible to conclusively establish the nature of bonding in these complexes by Mössbauer spectroscopy alone, some other technique such as X-ray photoelectron spectroscopy could help to resolve the problem [18, 62].

There seems to be a correlation between the linewidths and the structure of these chelates. Resonance effect studies indicate that most of the molecules studied exhibit strong intermolecular interactions as expected of β-diketonate complexes. There is very little, if any, connection between isomer shift and fluorescence intensity.

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[1] T. Moeller, D. F. Martin, L. C. Thompson, R. Ferrus, G. R. Feistel, and W. J. Randall, Chem. Rev. **65**, 1 (1965).

[2] T. Moeller, in: MTP Int. Rev. Sci., Inorg. Chem. Ser. 1, **Vol. 7**, 291 (1972).

[3] H. G. Friedman, Jr., G. R. Choppin, and D. G. Feuerbacher, J. Chem. Ed. **41**, 354 (1964).

[4] C. E. Myers, L. J. Norman, II, and L. M. Loew, Inorg. Chem. **17**, 1581 (1978) and the references therein.

[5] C. E. Myers, Inorg. Chem. **14**, 199 (1975).

[6] R. E. Sievers, Ed., NMR Shift Reagents, AP, New York 1973 and the references therein.

[7] A. A. Pinkerton and W. L. Earl, J. Chem. Soc. Dalton **1978**, 267 and the references therein.

[8] L. F. Lindoy and W. E. Moody, J. Amer. Chem. Soc. **99**, 5863 (1977) and the references therein.

[9] L. F. Lindoy, W. E. Moody, J. Lewis, and T. W. Matheson, J. Chem. Soc. Dalton **1976**, 1965.

[10] O. A. Gansow, P. A. Loeffler, R. E. Davis, M. R. Willcott, III, and R. E. Lenkinski, J. Amer. Chem. Soc. **95**, 3390 (1973).

[11] K. Street, Jr., and G. T. Seaborg, J. Amer. Chem. Soc. **72**, 2790 (1950).

[12] J. C. Eisenstein, J. Chem. Phys. **25**, 142 (1956).

[13] S. F. A. Kettle and A. J. Smith, J. Chem. Soc. (A), 688 (1967).

[14] K. A. Gschneidner, Jr., J. Less. Common. Metals **25**, 405 (1971) and the references terein.

[15] A. Streitweiser, Jun., D. Dempf, G. N. LaMar, D. G. Karraker, and N. Edelstein, J. Amer. Chem. Soc. **93**, 7343 (1971).

[16] C. K. Jørgensen, Modern Aspects of Ligand Field Theory, Chap. 23, Elsevier, New York 1971.

[17] C. K. Jørgensen, R. Pappalardo, and H. H. Schmidtke, J. Chem. Phys. **39**, 1422 (1963).

[18] R. Dubois, J. C. Carver, M. Tsutsui, and F. Lux, J. Coord. Chem. **6**, 123 (1976).

[19] P. Brix, S. Hufner, P. Kienle, and D. Quitmann, Phys. Lett. **13**, 140 (1964).

[20] S. Hufner, P. Kienle, D. Quitmann, and P. Brix, Z. Phys. **187**, 67 (1965).

[21] F. A. Deeney, J. A. Delaney, and V. P. Ruddy, Phys. Lett. **25** A, 370 (1967).

[22] G. Gerth, P. Kienle, and K. Luchner, Phys. Lett. **27** A, 557 (1968).

[23] F. A. Deeney, J. A. Delaney, and V. P. Ruddy, J. Inorg. Nucl. Chem. **30**, 1175 (1968).

[24] O. Berkooz, J. Phys. Chem. Sol. **30**, 1763 (1969).

[25] A. Z. Hrynkiewicz, D. S. Kulgawzuk, A. M. Pustowka, I. Stronski, and K. Tomala, J. Inorg. Nucl. Chem. **33**, 3707 (1971).

[26] H. U. Hrynkiewicz, A. Z. Hrynkiewicz, D. S. Kulgawczuk, K. Latka, A. J. Pustowka, I. Stronski, and K. Tomala, Proc. Conf. on Mössbauer Spectrometry, (Dresden 1971), Vol. 2, pp. 490.

[27] J. L. Mackey and N. N. Greenwood, J. Inorg. Nucl. Chem. **34**, 1529 (1972).

[28] P. Glentworth, A. L. Nichols, D. A. Newton, N. R. Large, and R. J. Bullock, J. Chem. Soc. Dalton **1973**, 546.

[29] M. F. Taragin and J. C. Eisenstein, J. Inorg. Nucl. Chem. **35**, 3815 (1973).

[30] S. Kumar, G. N. Rao, O. K. Medhi, and U. Agarwala, Z. Naturforsch. Teil **A 29**, 1778 (1974).

[31] A. H. Zaheer, I. B. Liss, N. B. Keck, W. G. Boss, and P. J. Ouseph, J. Inorg. Nucl. Chem. **36**, 2515 (1974).

[32] S. J. Lyle and A. D. Witts, J. Chem. Soc. Dalton **1975**, 185.

[33] C. M. P. Barton and N. N. Greenwood, in: Mössbauer Effect Data, Index, Covering the 1973 literature, Ed. by J. G. Stevens and V. E. Stevens, Plenum Publishing Corp., New York 1975, pp. 395–445.

[34] J. D. Cashion, M. A. Coulthard, and D. B. Prowse, J. Phys. C: Solid State Phys. **7**, 3620 (1974).

[35] J. D. Cashion, M. A. Coulthard, and D. B. Prowse, ibid **8**, 1267 (1975).

[36] J. D. Fackler, Jr., Prog. Inorg. Chem. **7**, 370 (1966). Ed. by F. A. Cotton, Interscience, New York 1966.

[37] E. L. Muetterties and C. M. Wright, J. Amer. Chem. Soc. **87**, 4706 (1965).

[38] J. K. Przystal, W. G. Boss, and I. B. Liss, J. Inorg. Nucl. Chem. **33**, 679 (1971).

[39] H. Bauer, L. R. Melby, N. J. Rose, E. Abramson, and J. C. Caris, J. Amer. Chem. Soc. **86**, 5117 (1964).

[40] R. E. Whan and G. A. Crosby, J. Mol. Spect. **8**, 315 (1962).

[41] R. G. Charles, J. Inorg. Nucl. Chem. **26**, 2195 (1964).

[42] N. K. Dutt and S. Sur, ibid **31**, 3171 (1969).

[43] A. K. Gupta, K. R. Sarma, J. J. Huntzikar, and G. N. Rao, Rev. Sci. Instruments **45**, 1423 (1974).

[44] D. A. Shirley, Rev. Mod. Phys. **36**, 339 (1964).

[45] H. H. Wickman, I. Nowik, J. H. Wernick, D. A. Shirley, and R. B. Frankel, J. Appl. Phys. **37**, 1246 (1966).

[46] M. A. Coulthard, J. Phys. B: Atom. Mol. Phys. **6**, 23 (1973).

[47] G. W. Dulaney and A F. Clifford, Mössbauer Effect Methodology (Ed. by I. J. Gruverman), **Vol. 5**, pp. 65–76. Plenum Press, New York 1969.

[48] S. P. Sinha, Europium, Springer-Verlag, New York 1967.

[49] S. I. Weissman, J. Chem. Phys. **10**, 214 (1942).

[50] N. Filipescu, W. F. Sagar, and F. A. Serafin, J. Phys. Chem. **68**, 3324 (1964).

[51] B. A. Goodman, N. N. Greenwood, and G. E. Turner, Chem. Phys. Lett. **5**, 181 (1970).

[52] S. A. Cotton and F. A. Hart, The Heavy Transition Elements (McMillan) 1975, pp. 208.
[53] M. A. Porrai-Koshits, L. A. Aslanov, L. A. Butman, A. L. Il'inskii, and E. F. Koritny, Acta Cryst. **A 25**, 5165 (1969).
[54] L. A. Aslanov, A. L. Il'inskii, I. I. Lazarev, and M. A. Porai-Koshits, J. Struct. Chem. **10**, 321 (1969).
[55] A. L. Il'inskii, M. A. Porai-Koshits, L. A. Aslanov, and P. I. Lazarev, J. Struct. Chem. **13**, 254 (1972).
[56] J. A. Cunningham, D. E. Sands, W. F. Wagner, and M. F. Richardson, Inorg. Chem. **8**, 22 (1969).
[57] J. G. White, Inorg. Chim. Acta **16**, 159 (1976).
[58] G. Lang, Nucl. Inst. Methods **24**, 425 (1963).
[59] R. G. Charles and R. C. Ohlmann, J. Chem. Phys. **40**, 3131 (1964).
[60] H. Samelson, A. Lempicki, V. A. Brophy, and C. Brecher, J. Chem. Phys. **40**, 2547 (1964).
[61] F. Halverson, J. S. Brinen, and J. R. Leto, J. Chem. Phys. **41**, 2752 (1964).
[62] M. A. Coulthard, J. Phys. B: Atom. Mol. Phys. **7**, 440 (1974).