

# Evidence of $Mn^{2+}$ - $Mn^{2+}$ Double Excitation transitions in $NH_4MnCl_3$ by pressure spectroscopy

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Double excitation (DE) transitions are investigated in  $NH_4MnCl_3$  microcrystals by high-pressure optical spectroscopy. Two intense bands observed at 39200 and 42200  $cm^{-1}$  in the UV absorption spectrum at room temperature are reported for the first time. The bands are assigned to the DE transitions  ${}^4T_{1g} + {}^4T_{1g}$  and  ${}^4T_{1g} + {}^4A_{1g} {}^4E_g$  on the basis of their pressure dependence. Apart from the DE energy as sum of the corresponding single excitation (SE) energies, the proposed assignment is clearly confirmed through the pressure shift rates. This procedure enables us to discard any other overlapping SE and DE transitions as responsible for the observed bands.

[Double excitation, Crystal field spectrum, Pressure spectroscopy, Mn(II),  $NH_4MnCl_3$  perovskite]

## 1. Introduction

This work investigates the existence of double excitations (DE) in the optical absorption (OA) spectrum of the  $NH_4MnCl_3$  perovskite through pressure techniques. The presence of DE bands in the electronic spectra of transition metal compounds is a rather unusual phenomenon that, in contrast to single excitations (SE), can not be explained on the basis of the isolated complex  $MX_6$  (M: transition ion; X: ligand). A DE is an electronic transition involving excited pair states and therefore can only occur in exchanged-coupled systems [1-5].

The aim for studying DE in  $Mn^{2+}$  systems is twofold. Firstly, they attract interest because a DE provides a direct way of simultaneously exciting two metal ions with one single photon. Their transition energy is close to the sum of the corresponding SE energies and therefore can exhibit large thermal or pressure shifts. This is worthwhile for  $Mn^{2+}$  systems since the involved excited states depend strongly on the crystal field splitting  $10Dq$  [6,7]. Interestingly, the presence of DE in the OA spectrum can lead to interesting piezochromic effects. Second, DE can be used as probes to detect aggregated phases in insulating materials through non-destructive techniques like optical spectroscopy. This latter aspect was exploited to identify precipitates in  $Mn^{2+}$ -doped alkali halides [8,9].

Although DE phenomena have been widely investigated in fluorides such as  $MnF_2$ ,  $KMnF_3$ ,  $RbMnF_3$  and  $BaMnF_4$  [1-4, 10-12], these optical transitions are much less known in chlorides, given that they appear near the absorption threshold and overlap with several  $Mn^{2+}$  SE of the same energy. The pioneering work carried out in  $Rb_2MnCl_4$  is an example of this behavior [13].

In this work we research DE transitions in  $NH_4MnCl_3$  by high pressure OA spectroscopy. This procedure has proved to be a powerful tool for revealing DE through the variations of energy induced by pressure. In particular, pressure shifts enable us to distinguish unambiguously the  ${}^6A_{1g} + {}^6A_{1g} \rightarrow {}^4T_{1g} + {}^4T_{1g}$  and  ${}^4T_{1g} + {}^4A_{1g} {}^4E_g$  DE from other overlapping DE and  ${}^6A_{1g} \rightarrow {}^4T_{1g}$  SE. The present method improves the usual procedures of assigning DE based on the transition energy and the variation of intensity with the temperature [11-13]

We select  $NH_4MnCl_3$  for this study because it is, together with  $TiMnCl_3$ , the only manganese trichloride with the perovskite structure at ambient conditions [7,14]. This structure is important to establish structural correlations in pressure experiments.

## 2. Experimental

Single crystals of  $NH_4MnCl_3$  were grown by the Bridgman technique from the melt at 481 °C. The  $Pm\bar{3}m$  cubic symmetry [14,15] was checked by X-ray diffraction and the optical quality by means of a polarizing microscope. The OA spectra under pressure were obtained by means of a single beam microspectrometer specially designed for use with Diamond Anvil Cells (DAC) [16]. This apparatus improved the signal to noise ratio by an order of magnitude with respect to a previously used standard setup [17], thus enabling to measure absorption bands with optical densities in the 0.01 to 5 range. The upper limit is significantly reduced below 300 nm due to the diamond absorption. A parallelepiped single crystal of  $100 \times 100 \times 30 \mu m^3$  was used in the pressure experiments. The pressure was applied with a DAC (High Pressure Diamond Optics, Inc) and calibrated through the Ruby R-line shift. Merck spectroscopic paraffin oil was employed as pressure transmitter in order to avoid moisture. The Ruby luminescence was excited with the 568-nm line of an I-302-K Coherent Krypton laser using the setup described elsewhere [16].

## 3. Results and discussion

### 3.1 Single Excitation transitions

Figures 1 and 2 depict the variation of the OA spectra of  $NH_4MnCl_3$  with pressure in the crystal field range and the UV threshold region, respectively. The three peaks observed in the spectra of Fig. 1 are characteristic of crystal field transitions of  $Mn^{2+}$  in an octahedral environment of Cl ligands:  $MnCl_6^{4-}$  complex. The analysis of these spectra in terms of the Racah parameters, B and C, and the crystal field parameters,  $10Dq$ , and their dependence with pressure has already been reported [18]. The three peaks appear at 19590, 22840 and 23935  $cm^{-1}$  at  $P=0$ , and correspond to SE from the  ${}^6A_{1g}$  electronic ground state to the  ${}^4T_{1g}$ ,  ${}^4T_{2g}$  and  ${}^4A_{1g} {}^4E_g$  excited states, respectively, arising from the  ${}^4G$  multiplet of  $Mn^{2+}$  split by the octahedral field in  $MnCl_6^{4-}$ . Fig. 3 plots the variation of the SE energies with the pressure.

The peak shifts of Fig. 1 reflect an increase of  $10Dq$  and a reduction of B and C upon pressure as a consequence of the metal-ligand distance decrease due to the crystal compression.

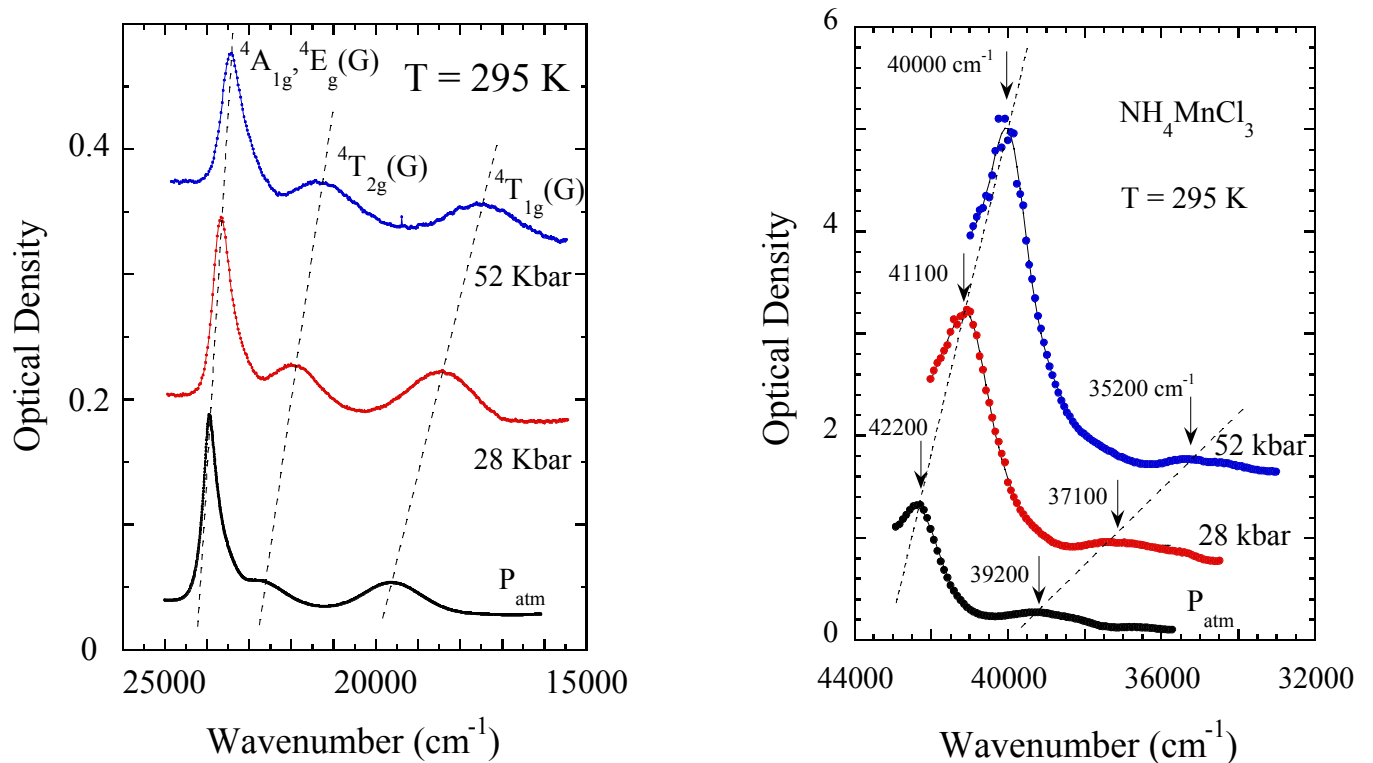


Fig. 1. Variation of the crystal field spectrum of  $\text{NH}_4\text{MnCl}_3$  with pressure. The bands are identified by the commonly used labels. Note the different pressure shift experienced by the three bands.

The larger red-shift experienced by  ${}^4\text{T}_{1g}$  and  ${}^4\text{T}_{2g}$  in comparison to  ${}^4\text{A}_{1g}{}^4\text{E}_g$  is due to the different pressure-dependence of the transition energies with  $10Dq$  according to the Tanabe-Sugano diagram for  $d^5$  ions [19]. Whereas the  ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}$  ( $-37 \text{ cm}^{-1}/\text{kbar}$ ) and  ${}^4\text{T}_{2g}$  ( $-28 \text{ cm}^{-1}/\text{kbar}$ ) transitions involve a change of the electronic configuration from  $t_{2g}^3 e_g^2$  to  $t_{2g}^4 e_g^1$ , and thus are nearly proportional to  $-10Dq$ , the spin-flip  ${}^6\text{A}_{1g} \rightarrow {}^4\text{A}_{1g}{}^4\text{E}_g$  transition does not change the electronic configuration and is  $10Dq$ -independent. The measured shift-rate of  $-9 \text{ cm}^{-1}/\text{kbar}$  for the latter transition is associated with the reduction of B and C upon pressure due to the increase of covalency of the Mn-Cl bond [7,18].

### 3.2 Double Excitation transitions

Apart from the weak SE of  $\text{Mn}^{2+}$ , the OA spectrum of  $\text{NH}_4\text{MnCl}_3$  (Fig. 2) shows a new band at  $39200 \text{ cm}^{-1}$  at zero pressure and room temperature, which was not detected in previous optical studies [15]. Its intensity is an order of magnitude higher than any SE intensity. The pressure red-shift of  $-4000 \text{ cm}^{-1}$  experienced by this band from 0 to 52 kbar, is twice the pressure red-shift undergone by the most shifted  ${}^4\text{T}_{1g}(\text{G})$  SE in the same pressure range. Interestingly, we also detect an intense band in the absorption threshold of the crystal. Its detection is a difficult task to accomplish given that it is located in the diamond absorption region, and the optical density at the band maximum is close to the sensitivity limit of the spectrometer. The band energy variation of these two UV bands with the pressure is shown in Fig. 4. Both the energy at  $P=0$  and the corresponding pressure shift-rate clearly indicate that these two bands at  $39200$  and  $42200 \text{ cm}^{-1}$  correspond the  ${}^4\text{T}_{1g} + {}^4\text{T}_{1g}$  and  ${}^4\text{T}_{1g} + {}^4\text{A}_{1g}{}^4\text{E}_g$  DE transitions, respectively.

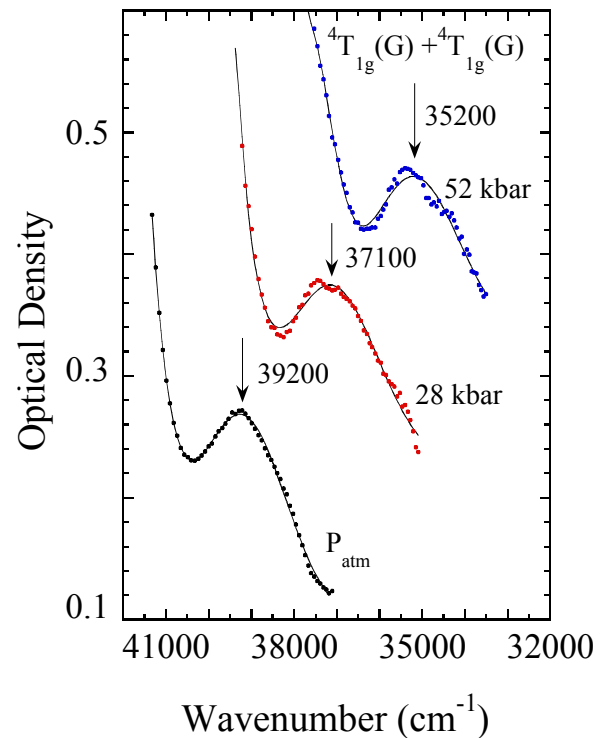


Fig. 2. (Top): Variation of the OA spectrum of  $\text{NH}_4\text{MnCl}_3$  in the UV region with pressure. Note the important pressure shift undergone by the two bands. The dotted straight lines are guides for the eyes. (Bottom) Magnification of the OA spectrum around the first UV band. Continuous lines are the least square fitting of data to two Gaussian bands.

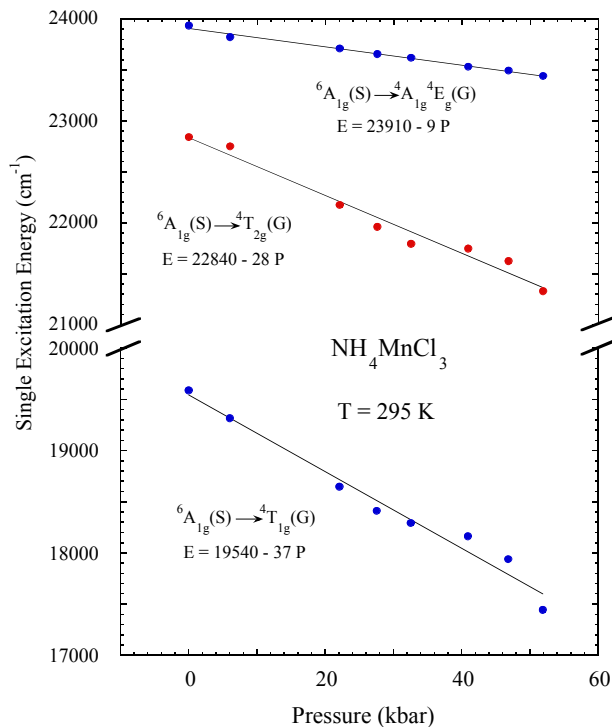


Fig. 3 Energy variation of the three crystal field bands in  $\text{NH}_4\text{MnCl}_3$  with the pressure. The straight lines represent the least-square linear fit.

The proposed assignment has been made on the basis that the  ${}^4\Gamma_i + {}^4\Gamma_j$  DE energy is close to the sum of the associated SE energies:

$$E({}^4\Gamma_i + {}^4\Gamma_j) = E({}^4\Gamma_i) + E({}^4\Gamma_j)$$

The first UV band at  $39200 \text{ cm}^{-1}$  therefore corresponds to a DE involving the first  ${}^4\text{T}_{1g}$  SE at  $19590 \text{ cm}^{-1}$ . In fact, both the energy and the pressure-shift rate of this band ( $\partial E/\partial P = -76 \text{ cm}^{-1}/\text{kbar}$ ) are twice the corresponding energy and shift rate of the  ${}^4\text{T}_{1g}(\text{G})$  SE ( $-37 \text{ cm}^{-1}/\text{kbar}$ ) such as is shown in Figs. 3 and 4.

It is worthwhile to point out that the calculated transition energies for the  ${}^4\text{T}_{1g}(\text{F})$ ,  ${}^4\text{T}_{2g}(\text{F})$  and  ${}^4\text{A}_{2g}(\text{F})$  SE of  $\text{Mn}^{2+}$  are in the  $38000 - 41000 \text{ cm}^{-1}$  range. However they can not be responsible for the observed UV bands given that they exhibit quite different  $10Dq$ -dependences. While transitions  ${}^6\text{A}_{1g}(\text{S}) \rightarrow {}^4\text{T}_{1g}(\text{F})$  and  ${}^4\text{T}_{2g}(\text{F})$  are mainly associated with change of electronic configuration from  $t_{2g}^3 e_g^2$  to  $t_{2g}^2 e_g^3$ , and are thus proportional to  $+10Dq$ , the  ${}^6\text{A}_{1g}(\text{S}) \rightarrow {}^4\text{A}_{2g}(\text{F})$  is  $10Dq$ -independent. Pressure spectroscopy is thus crucial to reveal DE phenomena. The UV band at  $42200 \text{ cm}^{-1}$  is a clear example of this behavior. The assignment of this band to a  $\text{Mn}^{2+}$  SE must be ruled out due to the large pressure red-shift of  $-48 \text{ cm}^{-1}/\text{kbar}$  (Fig. 4).

With regards to the transition energy at  $P=0$ , it could be related to the  ${}^4\text{T}_{1g} + {}^4\text{T}_{2g}$  DE since the energy is close to the sum of the corresponding SE energies:  $E({}^4\text{T}_{1g}) + E({}^4\text{T}_{2g}) = 42430 \text{ cm}^{-1}$ .

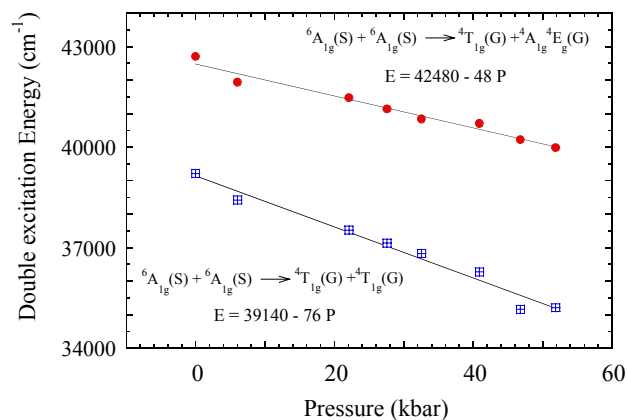


Fig. 4 Energy variation of the two UV bands in  $\text{NH}_4\text{MnCl}_3$  with the pressure. The equations and the straight lines correspond to the least-square linear fit of data. The labels show the proposed double excitation assignment.

An analogous band observed in the  $T=77 \text{ K}$  OA spectrum of  $\text{Rb}_2\text{MnCl}_4$  at  $41480 \text{ cm}^{-1}$  was assigned to the  ${}^4\text{T}_{1g} + {}^4\text{T}_{2g}$  DE using the precedent argument [13]. However, the band shape analysis of these UV bands strongly suggests that rather than  ${}^4\text{T}_{1g} + {}^4\text{T}_{2g}$ , the high-energy band seems to be associated with the  ${}^4\text{T}_{1g} + {}^4\text{A}_{1g}{}^4\text{E}_g$  DE. In fact, the intensity of the  $42200 \text{ cm}^{-1}$  band is an order of magnitude higher than the  ${}^4\text{T}_{1g} + {}^4\text{T}_{1g}$  DE at  $39200 \text{ cm}^{-1}$  in  $\text{NH}_4\text{MnCl}_3$ . Moreover, its bandwidth is half the  ${}^4\text{T}_{1g} + {}^4\text{T}_{1g}$  bandwidth. The comparison of these results (Fig. 2) with the corresponding DE observed in manganese fluorides [1-4,10-12], strongly supports the  ${}^4\text{T}_{1g} + {}^4\text{A}_{1g}{}^4\text{E}_g$  DE assignment. Furthermore, this is clearly confirmed by the pressure-induced band-shift of  $-48 \text{ cm}^{-1}/\text{kbar}$  (Fig. 4). In contrast to the assignment based on the DE energy at  $P=0$  as  $E({}^4\Gamma_i + {}^4\Gamma_j) = E({}^4\Gamma_i) + E({}^4\Gamma_j)$ , the use of the pressure shift-rate,  $\partial E/\partial P$ , is advantageous to distinguish the  ${}^4\Gamma_i + {}^4\Gamma_j$  DE related transition to this band. This is because the goodness of the  $E({}^4\Gamma_i + {}^4\Gamma_j) = E({}^4\Gamma_i) + E({}^4\Gamma_j)$  approximation depends on the magnitude of the two-exciton stabilization energy with respect to the sum of the SE energies. If we assume that this contribution is less than or equal to 5% the DE energy, then a DE assignment based on the transition energy may be insufficient. On the other hand, the pressure shift-rate results more accurate than the DE energy since the associated shift-rates for DE are quite different. Consequently, pressure shifts provide a direct way of assigning DE in terms of the parent SE transitions. The shift-rate of  $-48 \text{ cm}^{-1}/\text{kbar}$  measured for the absorption threshold clearly indicates that the involved DE is associated with  ${}^4\text{T}_{1g} + {}^4\text{A}_{1g}{}^4\text{E}_g$  transition. This value is close to the sum of the SE pressure-shifts:

$$\partial E({}^4\text{T}_{1g})/\partial P + \partial E({}^4\text{A}_{1g}{}^4\text{E}_g)/\partial P = (-37) + (-9) = -46 \text{ cm}^{-1}/\text{kbar}$$

and is rather different than the expected pressure shift for the previously assigned  ${}^4\text{T}_{1g} + {}^4\text{T}_{2g}$  DE:

$$\partial E({}^4\text{T}_{1g})/\partial P + \partial E({}^4\text{T}_{2g})/\partial P = (-37) + (-28) = -65 \text{ cm}^{-1}/\text{kbar}.$$

It must be noted that the present procedure of assigning DE can not be analogously applied to the thermal shifts. While the

expected pressure-shift for a given  ${}^4\Gamma_i + {}^4\Gamma_j$  DE is the sum of the  ${}^4\Gamma_i$  and  ${}^4\Gamma_j$  SE pressure-shifts, this is not necessarily true for the thermal shift:

$$\delta_T({}^4\Gamma_i + {}^4\Gamma_j) \neq \delta_T({}^4\Gamma_i) + \delta_T({}^4\Gamma_j)$$

The inequality is due to the explicit contribution  $[\partial E/\partial T]_V$  [20,21]. Thermal shifts at constant pressure can be expressed in terms of the energy derivatives with respect to the temperature as

$$[\partial E/\partial T]_P = [\partial E/\partial V]_T[\partial V/\partial T]_P + [\partial E/\partial T]_V$$

The first term (implicit contribution) represents the thermal shift associated with changes of volume by thermal expansion effects, whereas the second term (explicit contribution) accounts for band shifts induced by changes of temperature at constant volume. A detailed analysis of the different contributions to the thermal shift in  $\text{MnF}_6^{4-}$  systems is given elsewhere [21]. Although the implicit contribution to the DE thermal shift should be the sum of the SE shift like in pressure experiments, the explicit term, however, strongly depends on the difference between ground state and excited state vibrational frequencies [20,21]. Therefore the latter contribution can be similar for DE and the corresponding SE transitions. In  $\text{KMnF}_3$  and  $\text{RbMnF}_3$  [20], the implicit term represents 40% of the total thermal shift, thus  $\delta_T(\text{DE})$  is not necessarily the sum of the corresponding SE thermal shifts,  $\delta_T(\text{SE})$ . The comparison of the thermal shifts undergone by several DE bands and the corresponding SE bands in different manganese fluorides confirms this behavior [10-12].

#### 4. Conclusions

Throughout this work it is demonstrated that high pressure optical spectroscopy is a suitable tool to identify double excitation bands in the optical absorption spectrum of transition metal compounds. In particular, two new UV bands observed at 39200 and 42200  $\text{cm}^{-1}$  in  $\text{NH}_4\text{MnCl}_3$  have been assigned to the  ${}^4\text{T}_{1g}(\text{G}) + {}^4\text{T}_{1g}(\text{G})$  and  ${}^4\text{T}_{1g}(\text{G}) + {}^4\text{A}_{1g}{}^4\text{E}_g(\text{G})$  double excitations through their pressure-induced red-shift. The use of pressure spectroscopy has proved to be useful not only to distinguish DE from SE of the same energy in manganese compounds through their pressure shift, but also to elucidate among different DE appearing near the absorption threshold. The present method improves the assignment procedure based on the DE energy as sum of the corresponding SE energies. In  $\text{Mn}^{2+}$  systems, this procedure must be taken with caution if the two-exciton stabilization energy amounts 2-5% the DE energy. The comparison of the pressure shift rates of DE and SE provides an accurate DE assignment in terms of the parent SE transitions.

#### 5. Acknowledgements

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