

Normal Coordinate Analysis of Nitrogen trichloride

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The intramolecular force fields of nitrogen trichloride have been determined using the recent experimental data on the vibrational frequencies. Three different methods have been used for the evaluation of force constants. The results obtained are quite consistent.

Introduction

In a general program^{1,2} of determining the intramolecular force field of Group V trihalides the NCl_3 molecule could not be studied for the lack of experimental data. Nitrogen trichloride belongs to the C_{3v} point group having pyramidal structure with two non-degenerate vibrations belonging to A_1 -species and two degenerate vibrations belonging to E-species. CARTER et al.³ have, recently, reported the fundamental frequencies of this molecule and it was thought worthwhile to calculate its force constants and related properties.

DUNCAN⁴ has shown that the simple Urey-Bradley Force Field (UBFF) is not capable of satisfactorily explaining the vibrations of pyramidal XY_3 molecules, as it does not take into account the interactions between two angle bendings and bond stretching and angle bending when the bond is not continuous, with the angle. A modified UBFF was suggested by SHIMANOUCI et al.⁵ to improve this situation by introducing cross terms for bond-angle and angle-angle interactions. In a recent paper CARTER et al.⁶ have proved the utility of this modified UBFF for NCl_3 . In an attempt to describe the normal vibrations of NH_3 PARISEAU et al.⁷ suggested the inclusion in the potential field of the repulsion between a ligand atom and the lone-pair of electrons on the central atom. The lone-pair acts as a virtual atom of zero mass. The same

method has been applied to NF_3 by CURTIS and MUIRHEAD⁸ and to the group V trihalides by KING and OVEREND⁹. These studies have proven the general superiority of the lone-pair model in describing the vibrations of pyramidal molecules over the simple UBFF. Our aim is to see how well this model works in the case of NCl_3 .

While this work was in process, BAYERSDORFER et al.¹⁰ carried out GVFF calculations for this molecule. In the present communication we have applied three different models for the potential field, namely, an approximate GVFF, simple UBFF and lone-pair model, for the evaluation of force constants of the molecule.

Methods of Calculations

The symmetry coordinates used in the present calculations are the same as those given in¹ and². There have not been any structural investigations on this molecule and the bond length was estimated from the relation:

$$\begin{aligned} \text{N-Cl (in } \text{NCl}_3\text{) / N-F (in } \text{NF}_3\text{)} \\ &= \text{P-Cl (in } \text{PCl}_3\text{) / P-F (in } \text{PF}_3\text{)}, \\ &= \text{As-Cl (in } \text{AsCl}_3\text{) / As-F (in } \text{AsF}_3\text{)}. \end{aligned}$$

The mean value of the N-Cl bond length is thus found to be 1.78 Å. This is in good agreement with its approximate value (1.73 Å) obtained from the relation¹¹:

$$r = r_{\text{N}} + r_{\text{Cl}} - 0.06 | \chi_{\text{N}} - \chi_{\text{Cl}} |$$

where r_{N} and r_{Cl} are the atomic radii and χ_{N} and χ_{Cl} are the electronegativities. The bond angle has been assumed to be 100° . The bond angle has also been estimated like the bond length i. e. from the relation

$$\begin{aligned} < \text{ClNCl (in } \text{NCl}_3\text{) / } < \text{FNF (in } \text{NF}_3\text{)} \\ &= < \text{ClPcl (in } \text{PCl}_3\text{) / } < \text{FPF (in } \text{PF}_3\text{)} \text{ etc.} \end{aligned}$$

The expressions for symmetrized force constants in terms of the parameters entering in the three methods are given in Table 1, where "r" refers to the N-Cl bond and "α" to Cl-N-Cl angle.

Table 1. F-Matrix Elements in Different Force Fields for NCl_3 .

| F-Matrix Elements | GVFF | Simple UBFF | Lone Pair Model |
|---------------------------------|-------------------------|---|--|
| A_1 Species | | | |
| F_{11} | $f_r + 2 f_{rr}$ | $K + 4 F \sin^2 \frac{1}{2} \alpha$ | $K_r + 4 F_r \sin^2 \frac{1}{2} \alpha$ |
| F_{12} | $r(2 f_{ra} + f_{ra}')$ | $1.8 r F \sin \frac{1}{2} \alpha \cos \frac{1}{2} \alpha$ | $r[0.9 F_r \sin \frac{1}{2} \alpha \cos \frac{1}{2} \alpha + 3 F_{ra}]$ |
| F_{22} | $r^2(f_a + 2 f_{aa})$ | $r^2[H + F(\cos^2 \frac{1}{2} \alpha + 0.1 \sin^2 \frac{1}{2} \alpha)]$ | $[H_a + F_r(\cos^2 \frac{1}{2} \alpha + 0.1 \sin^2 \frac{1}{2} \alpha)] r^2$ |
| E Species | | | |
| F_{33} | $f_r - f_{rr}$ | $K + F[\sin^2 \frac{1}{2} \alpha - 0.3 \cos^2 \frac{1}{2} \alpha]$ | $K_r + F_r[\sin^2 \frac{1}{2} \alpha - 0.3 \cos^2 \frac{1}{2} \alpha]$ |
| F_{34} | $r(-f_{ra} + f_{ra}')$ | $r[0.9 F_r \sin \frac{1}{2} \alpha \cos \frac{1}{2} \alpha]$ | $r[0.9 F_r \sin \frac{1}{2} \alpha \cos \frac{1}{2} \alpha]$ |
| F_{44} | $r^2(f_a - f_{aa})$ | $r^2[H + F(\cos^2 \frac{1}{2} \alpha + 0.1 \sin^2 \frac{1}{2} \alpha)]$ | $[H_a + F_r(\cos^2 \frac{1}{2} \alpha + 0.1 \sin^2 \frac{1}{2} \alpha)] r^2$ |

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The set of symmetrized force constants using the L -matrix approximation method have been calculated from the following relations given by PEACOCK and MÜLLER¹²:

$$F_{ii} = \frac{D \lambda_i + G_{ij}^2 \lambda_j}{G_{ii} D}; \quad F_{ij} = -\frac{G_{ij} \lambda_j}{D}; \quad F_{jj} = \frac{G_{ii} \lambda_j}{D}$$

where $D = \det |G|$ and λ_i, λ_j are the eigenvalues of the secular equation related to the vibrational frequencies ν_i, ν_j . The approximate GVFF calculated from these

Table 2. Observed and calculated vibrational frequencies (cm^{-1}) for NCl_3 .

| i | ν_i Observed | ν_i Calculated Lone Pair Model | ν_i Calculated Simple UBFF | $\Delta \nu_i$ % Lone Pair Model | $\Delta \nu_i$ % Simple UBFF |
|-----|---------------------|---|--------------------------------------|--|------------------------------------|
| 1 | 538 | 519.7 | 592.7 | 3.41 | -10.17 |
| 2 | 349 | 336.7 | 343.1 | 3.52 | 1.70 |
| 3 | 642 | 659.5 | 659.1 | -2.72 | -2.67 |
| 4 | 258 | 266.5 | 254.5 | -3.31 | 1.35 |

$$\text{N. B.:} \quad \Delta \nu_i \% = \frac{\nu_{\text{obs.}} - \nu_{\text{calc.}}}{\nu_{\text{obs.}}} \times 100.$$

relations are quite reliable in the XY_n type molecules with $m_X > m_Y$ ¹³ but in the present case ($m_Y > m_X$) it is not very accurate and a slight correction¹⁴ is needed. However, this correction leads to imaginary force constants in A_1 -species in the present case. The limiting values of the force constants are obtained and given in parentheses in Table 3 which contains the results obtained from the above relations. In E-species the correction yields real force constants and Table 3 includes them also (in parentheses).

Table 3. Symmetrized force constants in $\text{mdyn}/\text{Å}$ (constants have been scaled with bond length) for NCl_3 .

| | F_{11} | F_{12} | F_{22} | F_{33} | F_{34} | F_{44} |
|---------------------------------|----------|----------|----------|----------|----------|----------|
| L Matrix approximation method | 3.54 | 0.79 | 0.51 | 2.50 | 0.37 | 0.42 |
| Simple UBFF | (2.58) | (0.60) | (0.61) | (2.19) | (0.22) | (0.44) |
| Lone Pair Model | 2.67 | 0.49 | 0.62 | 1.62 | 0.24 | 0.62 |
| Lone Pair Model | 2.94 | 0.63 | 0.49 | 2.18 | 0.18 | 0.49 |

In UBFF, we have to determine only three force constants from four known frequencies and therefore the problem is overdetermined. An iterative least squares treatment suggested by MANN et al.¹⁵, was employed using a judiciously chosen initial set of force constants. It was, however, not possible to get satisfactory results since the choice of different sets of initial constants led to slightly different converged force con-

stants. The constants summarized in Table 4 refer to the mean values of a number of such attempts. In the lone-pair model, there are four constants to be determined from four known vibrational frequencies but the direct solution of the problem leads to complex values for the force constants. We have, therefore, used the least squares adjustment technique referred to above

Table 4. Force constants for NCl_3 .

| | K or K_r ($\text{mdyn}/\text{Å}$) | H or H_a ($\text{mdyn-Å}/r^2$) | F or F_r ($\text{mdyn}/\text{Å}$) | F_{ra} ($\text{mdyn}/\text{Å}$) |
|-----------------|--|---|--|--|
| Simple UBFF | 1.36 | 0.35 | 0.55 | |
| Lone Pair Model | 2.00 | 0.30 | 0.40 | 0.15 |

for evaluating the force constants. The force constants thus obtained are expected to be more reliable than those obtained from the simple UBFF since the same set of converged force constants was obtained with different choices of the initial set in the present method.

Results and Discussions

The symmetrized force constants calculated by L -matrix approximation method, the simple UBFF and the lone-pair model have been summarized in Table 3. The symmetrized force constants obtained by L -matrix approximation are considerably larger than those obtained by the other two methods. This may be due to the appreciable mixing of two modes in the same species. An empirical correction¹⁴ has already been suggested to calculate force constants in such cases. However, in the preceding section we have seen that this correction leads to imaginary force constants in A_1 -species. Interestingly in E-species this correction gives real force constants which are in good agreement with the results obtained by the lone-pair model. The limiting values of the force constants in A_1 -species also lead to the same conclusion. Indeed, still more modifications are needed to improve the applicability of L -matrix approximation method but due to the non-availability of additional data we can not suggest any such modification at present.

The results of the lone-pair model are nearer to the results of GVFF (approximate) than the results of simple UBFF. The percentage deviations between the observed and calculated frequencies are shown in Table 2. We are led to the conclusion that the lone-pair model is a better approximation than the simple UBFF to fix the vibration frequencies.

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On the Application of OVFF to MX_6 Type Ions

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Force constants for nine ions belonging to O_h point group have been evaluated by using Orbital Valence Force Field. The constants have been compared with their values obtained by using Urey-Bradley Force Field. The validity of the two methods has been discussed.

Introduction

Simplified force fields such as Urey-Bradley Force Field (UBFF) and Orbital Valence Force Field (OVFF) play very important roles in the determination of molecular force fields of polyatomic molecules, specially when additional experimental data e. g. Coriolis coupling constants or frequencies of isotopic species are not available. Thus it becomes necessary to test carefully the validity of these model force fields and to assess their relative merits. Recently, KIM et al.¹ have emphasized the applicability of OVFF and have shown its superiority over UBFF in hexafluorides. We have also been interested in the studies of MX_6 type molecules and ions possessing O_h symmetry to see whether the superiority of the OVFF over UBFF claimed by KIM et al.¹ in hexafluorides holds in hexachlorides and hexabromides also and have shown in a recent paper² that it does not hold. However, in the previous paper² only a limited number of ions and one molecule were studied, it was thought worthwhile to extend the work. In the present communication the OVFF has been applied to nine ions. THAKUR et al.³ have already reported the UBFF constants for these ions. An attempt has been made to judge the suitability of these two model force fields for different hexahalides.

Method of Calculations

The elements of the kinetic and potential energy matrices used by us are the same as reported in our earlier paper². The vibrational frequencies for the first six ions i. e. PF_6^- , AsF_6^- , SbF_6^- , SiF_6^{--} , GeF_6^{--} , SnF_6^{--} , have been given by BEGUN and RUTENBERG⁴, and data for the remaining ions i. e. $ReCl_6^{--}$, $ReBr_6^{--}$, $OsCl_6^{--}$ were taken from NAGARAJAN's paper⁵. An initial set of force constants was obtained by an educated guess. This set was refined using the weighted least squares process described by MANN et al.⁶. The elements of the Jacobian matrix were calculated by giving an increment of 0.01 mdyn/A to each of the force constants in turn and determining the corresponding changes in frequencies. A new Jacobian was constructed after each iteration and the process repeated. Convergence was obtained usually after three or four itera-

Table 1. OVFF constants (in mdyn/A) for some MX_6 type ions.

| Molecule | K | D | F | F' |
|---------------|----------------|------------------|----------------|------------------|
| PF_6^- | 2.71 (2.95) | 0.86 (0.11) | 0.88 (0.92) | 0.03 (-0.14) |
| AsF_6^{--} | 3.12 (3.46) | 0.49 (0.13) | 0.52 (0.42) | 0.00 (-0.11) |
| SbF_6^{--} | 3.69 (3.69) | 0.00 (-0.03) | 0.32 (0.33) | -0.19 (-0.22) |
| SiF_6^{--} | 2.03 (2.06) | 0.27 (0.05) | 0.72 (0.73) | -0.07 (-0.10) |
| GeF_6^{--} | 2.16 (2.16) | 0.16 (0.00) | 0.52 (0.55) | -0.06 (-0.09) |
| SnF_6^{--} | 2.41 (2.55) | 0.01 (0.06) | 0.35 (0.33) | -0.07 (-0.15) |
| $ReCl_6^{--}$ | 1.38 (1.37) | -0.07 (-0.03) | 0.27 (0.27) | -0.03 (-0.06) |
| $ReBr_6^{--}$ | 1.06 (1.03) | 0.10 (-0.03) | 0.23 (0.29) | 0.00 (-0.04) |
| $OsCl_6^{--}$ | 1.31 (1.52) | 0.04 (0.00) | 0.28 (0.21) | -0.01 (-0.07) |

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Table 2. Observed and calculated vibrational frequencies (in cm^{-1}).

| Ions | ν_1 (A_{1g}) | $\Delta\nu_1$ % | ν_2 (E_g) | $\Delta\nu_2$ % | ν_3 (F_{1u}) | $\Delta\nu_3$ % | ν_4 (F_{1u}) | $\Delta\nu_4$ % | ν_5 (F_{2g}) | $\Delta\nu_5$ % |
|----------------------|----------------------|-----------------|-------------------|-----------------|----------------------|-----------------|----------------------|-----------------|----------------------|-----------------|
| PF_6^- | obs. 751 | 0.40 | 580 | 0.69 | 830 | -0.72 | 558 | 0.71 | 477 | -0.21 |
| | calc. 748 | | 576 | | 836 | | 554 | | 478 | |
| AsF_6^- | obs. 685 | 0.29 | 576 | 1.04 | 699 | -1.14 | 392 | 1.02 | 372 | 0.02 |
| | calc. 683 | | 570 | | 707 | | 388 | | 371 | |
| SbF_6^- | obs. 668 | 0.30 | 558 | 0.72 | 669 | -1.04 | 350 | 2.28 | 294 | -2.72 |
| | calc. 666 | | 554 | | 679 | | 342 | | 302 | |
| SiF_6^{--} | obs. 663 | 0 | 477 | 0 | 741 | -0.54 | 483 | 0.41 | 408 | 0 |
| | calc. 663 | | 477 | | 745 | | 481 | | 408 | |
| GeF_6^{--} | obs. 624 | 1.12 | 471 | 0.63 | 603 | -1.16 | 359 | 2.23 | 335 | -2.39 |
| | calc. 617 | | 468 | | 610 | | 351 | | 343 | |
| SnF_6^{--} | obs. 592 | 1.35 | 477 | 0 | 559 | -1.43 | 300 | 2.00 | 252 | -9.52 |
| | calc. 584 | | 477 | | 567 | | 294 | | 276 | |
| ReCl_6^{--} | obs. 346 | 0 | 275 | 0 | 313 | -1.91 | 172 | 11.04 | 159 | -1.26 |
| | calc. 346 | | 275 | | 319 | | 153 | | 161 | |
| ReBr_6^{--} | obs. 213 | 3.29 | 174 | 4.60 | 217 | 2.76 | 118 | 4.24 | 104 | -4.81 |
| | calc. 206 | | 166 | | 223 | | 113 | | 109 | |
| OsCl_6^{--} | obs. 346 | 0.29 | 274 | -0.36 | 314 | -0.63 | 177 | 3.95 | 165 | -6.66 |
| | calc. 345 | | 275 | | 316 | | 170 | | 176 | |

N. B.: $\Delta\nu_i$ % = $(\nu_{\text{obs.}} - \nu_{\text{calc.}}) / \nu_{\text{obs.}} \times 100$.

tions. The calculated OVFF constants are summarized in Table 1, along with the UBFF constants (given in parentheses) reported by THAKUR et al.³ The percentage errors in the calculated frequencies have been given in Table 2 which contains the observed and the calculated frequencies.

Results and Discussions

The OVFF constants reported in this paper seem physically meaningful and it is clear from Table 1 that they compare well with the UBFF constants reported earlier by THAKUR et al.³ It may be also seen that symmetrized force constants obtained by the OVFF constants are in good agreement with their values reported by RAO⁷ calculated by the use of extremal properties of the force constants. Bending force constants are negative for SiF_6^{--} and ReCl_6^{--} but they are very small in magnitude and hence they do not mar the physical significance of the constants.

It is obvious from Table 2 that the percentage errors in calculated frequencies are very small in hexa-

fluorides. It should be mentioned here that the UBFF method³ introduces comparatively larger errors than those due to the OVFF method in these hexafluorides. Thus it may be safely stated that the superiority of the OVFF over the UBFF as claimed by KIM et al.¹ holds in hexafluorides. However, it may be seen from Table 2 that for hexachlorides and hexabromides, both models are equally effective. The same conclusion has already been drawn by us². It is also important to point out that the errors are larger in bending frequencies than stretching frequencies. The number of ions or molecules studied by us is very limited as yet and so it is still highly desirable to study a large number of cases before one may arrive at a certain conclusion about the suitability of these two model force fields to fix the vibrational frequencies.

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Elektrisches Dipolmoment von InCl

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Electric Dipole Moment of InCl

Stark-effect measurements on the rotational transition $J=1 \rightarrow 2$ of InCl are described. The vapour pressure in the absorption cell was chosen so that the quadrupole hyperfine structure due to the Cl-nucleus could not be resolved. Thus we neglect this coupling in the calculation of the Stark-effect. The derived electric dipole moment in the ground vibrational state is:

$$^{115}\text{In}^{35}\text{Cl} : |\mu_0| = (3.79 \pm 0.10) \text{ D.}$$

The electric dipole moment of $^{205}\text{Tl}^{19}\text{F} : |\mu_0| = 4.2282(8) \text{ D}$ was used for the calibration of the electric field.

Kürzlich haben wir über Messungen des elektrischen Dipolmoments an TlBr und TlI¹ berichtet. Mit dieser Arbeit soll die systematische Untersuchung an zweiatomigen (III/VII)-Verbindungen durch eine entsprechende Messung im Rotationspektrum des InCl fortgesetzt werden. Diese Experimente innerhalb einer ganzen Klasse von Molekeln haben das Ziel, Vergleiche von isoelektronischen Molekülgruppen vornehmen zu können und daraus gemeinsame Züge der molekularen Konstanten abzuleiten. Erste Hinweise dazu haben wir in einer Studie über die zweiatomigen (IV/VI)-Verbindungen² erhalten; die Gruppe der (III/VII)-Molekeln ist isoelektronisch dazu.

Die Experimente werden mit dem gleichen Stark-Effekt-Mikrowellenspektrometer durchgeführt, wie es schon in ¹ benutzt wurde und näher in ³ beschrieben ist. In und Cl haben beide einen Kernspin $I \geq 1$, so daß InCl Quadrupolhyperfeinstruktur (HFS) von beiden Kernen zeigt. Diese HFS ist seit langem bekannt, die neueste Auswertung⁴ ergibt Quadrupolkopplungskonstanten im Schwingungsgrundzustand zu:

$$^{115}\text{In} : e q_0 Q = -657,52(50) \text{ MHz,}$$

$$^{35}\text{Cl} : e q_0 Q = -13,63(20) \text{ MHz.}$$

Da die Cl-HFS hinreichend klein ist, gelingt es durch entsprechende Wahl der Temperatur, den Dampfdruck von InCl so einzustellen, daß die Druckverbreiterung gerade die Cl-Aufspaltung verschmiert. Dadurch wird es möglich, die Auswertung des Stark-Effekt-Spektrums unter Vernachlässigung der Cl-HFS vorzunehmen. Man

muß nur noch dafür sorgen, daß die für die Messung verwendeten elektrischen Felder groß genug sind, um bezüglich der Cl-Hyperfeinkopplung im Fall des starken Feldes zu sein. Dann ergeben sich symmetrisch durch die nichtaufgelöste Struktur verbreiterte Absorptionslinien, und systematische Verschiebungen des Linienschwerpunktes durch die Cl-Hyperfeinenergien sind innerhalb unserer Meßgenauigkeit zu vernachlässigen.

InCl ist im festen Zustand hinreichend stabil, so daß es separat hergestellt werden kann. Bei Temperaturen von 200 °C verdampft unter Vakuum InCl aus einem Gemisch von InCl₃ und In und kondensiert an einem wassergekühlten Finger mit oranger Farbe. Dieses Präparat wird erneut in der Absorptionszelle verdampft.

Bei Temperaturen um 250 °C wurde der Rotationsübergang $J = 1 \rightarrow 2$, $F_1 = 11/2 \rightarrow 13/2$ im Schwingungszustand $v=0$ beobachtet. F_1 ergibt sich aus der Kopplung des Rotationsdrehimpulses J mit dem Kernspin $I_1 = 9/2$ des Indiums; F_1 ist also nicht der Gesamtdrehimpuls. Entsprechend der in ¹ beschriebenen Auswertemethode wurde der Übergang mit maximalem F_1 zu jedem J gewählt und schließlich der Stark-Übergang mit maximalem $|M_{F_1}| = I_1 + J$ vermessen. Das bedeutet hier $|M_{F_1}| = 11/2 \rightarrow 13/2$.

Die entsprechenden Eigenwerte berechnen sich aus einer eindimensionalen Matrix¹. Die benötigte Rotationskonstante B_v wird der Arbeit⁴ entnommen.

Der Schwerpunkt des Überganges $J, F_1 = 1, 11/2 \rightarrow 2, 13/2$ im feldfreien Raum wurde auf zwei verschiedene Arten ermittelt. Im Fall 1 wurde ein Mittelwert aus mehrfachen Messungen des druckverbreiterten Überganges bestimmt. Die volle Halbwertsbreite betrug hier 1,1 MHz. Im Fall 2 wurde bei verminderter Temperatur die Cl-HFS dieses Überganges aufgelöst. Bei einer vollen Halbwertsbreite von etwa 150 kHz beobachtet man 4 Linien zu $\Delta F = +1$. Die Übergänge zu $\Delta F = 0$ oder $\Delta F = -1$ wurden nicht gemessen, da ihre Intensität mehr als einen Faktor 20 gegenüber den Linien mit $\Delta F = +1$ kleiner ist. Die relativen Intensitäten I dieser Übergänge wurden mit der in ⁴ angegebenen Methode bestimmt und sind so normiert, daß die Summe über alle HFS-Übergänge eines Schwingungszustandes 100% ergibt. Aus den hier gemessenen Linien und den Intensitäten wird schließlich der Schwerpunkt bestimmt. Beide Verfahren liefern das gleiche Ergebnis, wie es in Tab. 1 zusammengestellt ist. Gegenüber dieser Schwerpunktsfrequenz wird die Frequenzverschiebung $\Delta\nu$ durch den Stark-Effekt am Übergang $|M_{F_1}| = 11/2 \rightarrow 13/2$ berechnet.

Zur Eichung des elektrischen Feldes in der heißen Zelle wird TlF benutzt, dessen Dipolmoment aus Mes-

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Tab. 1. Schwerpunktsfrequenzen des Überganges $v=0$; $J, F_1=1, 11/2 \rightarrow 2, 13/2$ im feldfreien Raum am $^{115}\text{In}^{35}\text{Cl}$.

| Fall 1 | | $\nu_s = 13061,190$ (40) MHz | |
|--------|--------------------|------------------------------|---------|
| Fall 2 | $F \rightarrow F'$ | ν (MHz) | I (%) |
| | 6 \rightarrow 7 | 13060,740 (15) | 7,28 |
| | 5 \rightarrow 6 | 13061,044 (15) | 6,11 |
| | 7 \rightarrow 8 | 13061,411 (15) | 8,50 |
| | 4 \rightarrow 5 | 13061,663 (15) | 5,19 |
| | | $\nu_s = 13061,196$ (20) MHz | |

sungen von v. BOECKH⁵ et al. mit Hilfe der elektrischen Molekülstrahlresonanz sehr genau bekannt ist. Es erwies sich als unmöglich, InCl und TlF gleichzeitig in der heißen Absorptionzelle zu beobachten; die Zersetzung beider Moleküle ist sehr stark. Deswegen mußte die Eichung unmittelbar nach der eigentlichen Messung an InCl vorgenommen werden. Dazu wurde die Zelle abgeheizt, die Eichsubstanz TlF ohne Demontage und größere Erschütterungen der Zelle eingefüllt und schließlich auf die Arbeitstemperatur wieder

Tab. 2. Einzelmessungen des elektrischen Dipolmoments von $^{115}\text{In}^{35}\text{Cl}$ im Schwingungsgrundzustand.

| $ \mu_0 $ (D) | $ \mu_0 $ (D) | $ \mu_0 $ (D) | $ \mu_0 $ (D) |
|-------------------------------|---------------|---------------|---------------|
| 3,741 | 3,805 | 3,837 | 3,805 |
| 3,759 | 3,819 | 3,811 | 3,796 |
| 3,796 | 3,768 | 3,812 | 3,795 |
| 3,756 | 3,813 | 3,762 | 3,736 |
| 3,770 | 3,801 | 3,780 | 3,789 |
| 3,817 | 3,835 | 3,770 | 3,775 |
| 3,800 | 3,851 | 3,780 | 3,767 |
| $ \mu_0 = (3,79 \pm 0,10)$ D | | | |

aufgeheizt. Zur Stabilisierung der Geometrie der Zelle wurde zusätzlich im heißen Bereich ein Quarzabstandsstück eingesetzt. Die Zuverlässigkeit eines solchen Vorgehens ergibt sich aus der Konsistenz mehrerer Meßreihen, wie sie in Tab. 2 angegeben sind.

Bei Feldern zwischen 360 und 440 V/cm wurden Frequenzverschiebungen $\Delta\nu$ gegen die Schwerpunktsfrequenz von 3,2 bis 4,9 MHz erzielt. Dabei beobachtet man keine wesentliche Verbreiterung des Stark-Überganges gegenüber der ungestörten Linie durch Feldinhomogenitäten. Das Signal-Rausch-Verhältnis der Stark-Übergänge betrug etwa 3 : 1 bei einer Zeitkonstanten des Verstärkerkanals von 1 sec. Tabelle 2 enthält auch den Mittelwert über alle Einzelmessungen des Dipolmoments, deren Fehler mit etwa 4% anzusetzen ist. Der angegebene Fehler des Mittelwerts ist wesentlich größer als der, den man aus der Streuung der Einzelwerte erhalten würde. Wir glauben, daß die Eichung des elektrischen Feldes in diesem Fall nicht die entsprechende absolute Genauigkeit erreicht, um den Fehler durch zahlreiche Einzelmessungen zu reduzieren.

Um die Vernachlässigung der Cl-HFS bei der Berechnung der Stark-Energien auch experimentell zu rechtfertigen, wurde eine Kontrollmeßreihe am $^{115}\text{In}^{37}\text{Cl}$ durchgeführt. ^{37}Cl hat einen kleineren eqQ -Wert als ^{35}Cl , da die beiden Kernquadrupolmomente ein Größenverhältnis haben von:

$$Q(^{35}\text{Cl})/Q(^{37}\text{Cl}) = 1,2688773(15)^6.$$

Aus dieser Meßreihe ergab sich ein elektrisches Dipolmoment im Schwingungsgrundzustand zu:

$$^{115}\text{In}^{37}\text{Cl} : |\mu_0| = 3,84(15) \text{ D}.$$

Dies ist in guter Übereinstimmung mit dem Wert für $^{115}\text{In}^{35}\text{Cl}$. Isotopieeffekt oder Einflüsse der Nullpunktschwingung sollten sich bei dieser Meßgenauigkeit noch nicht bemerkbar machen.

¹ E. TIEMANN, Z. Naturforsch. **26 a**, 1809 [1971].

² J. HOEFT, F. J. LOVAS, E. TIEMANN u. T. TÖRRING, J. Chem. Phys. **53**, 2736 [1970].

³ J. HOEFT, F. J. LOVAS, E. TIEMANN u. T. TÖRRING, Z. Angew. Phys. **31**, 265 [1971].

⁴ B. SCHENK, E. TIEMANN u. J. HOEFT, Z. Naturforsch. **25 a**, 1827 [1970].

⁵ R. v. BOECKH, G. GRÄFF u. R. LEY, Z. Phys. **179**, 285 [1964].

⁶ J. H. HOLLOWAY, Ph. D. Thesis, Massachusetts Institute of Technology, Cambridge, Mass. 1956.